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VAPOR-LIQUID EQUILIBRIA IN THE CARBON
DIOXIDE-N-HEXANE SYSTEM

BY

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A THESIS

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "Vapor-Liquid Equilibria in the Carbon Dioxide-N-Hexane System" submitted by B.N. Gupta in partial fulfilment of the requirements for the degree of Master of Science in Chemical Engineering.

ABSTRACT

A search through the literature on the vapor-liquid equilibria of carbon dioxide-paraffin hydrocarbon systems has indicated that there are no data available for binary systems of carbon dioxide between n-pentane and n-decane.

To bridge this gap, experimental vapor-liquid equilibrium data have been obtained for the carbon dioxide-n-hexane system. A variable volume windowed Jerguson gauge using mercury as the confining fluid was used for this purpose. The study was conducted at temperatures of 100, 150, 200, 250 and 300°F using five mixtures containing 94.9, 90.7, 84.6, 75.7 and 52.5 mole percent carbon dioxide.

The phase diagram was defined over the entire temperature range of the investigation. The phenomenon of critical opalescence was observed for some mixtures and this helped in defining the critical locus for the system.

A comparison of the n-hexane K-values with ideal K-values and those presented in the NGPSA Engineering Data Book has been made. The agreement between the experimental and the ideal K-values was better at higher temperatures. The NGPSA K-values showed good agreement with the experimental values at 200°F.

Such comparisons could not be made for the carbon dioxide K-values. However, the available data in the literature on the K-values of carbon dioxide in paraffin hydrocarbon systems were compiled. Charts have been prepared for the K-values of

this component at convergence pressures of 1200, 1450 and 1700 psia. At the convergence pressure of 1200 psia, the correlation of K-values obtained from data on many different carbon dioxide binaries is not good at temperatures 100°F and above. At the other two convergence pressures, however, the charts are similar in shape to those presented in the NGPSA Engineering Data Book.

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I. INTRODUCTION

A knowledge of the composition and amounts of the co-existing phases under heterogeneous equilibrium conditions is essential for good design of fractionating columns, absorbers and other contacting equipment. In the design of pipelines and storage tanks, it is usually desirable to avoid the formation to two phases. A priori knowledge of the vapor-liquid equilibria for the system under consideration is essential for this purpose. A knowledge of vapor-liquid equilibria is also very useful in predicting the performance of underground petroleum reservoirs.

A considerable amount of data has been accumulated over the years from the numerous investigations in the field of vapor-liquid equilibrium. Nevertheless, little or no information is available for many systems. Though methods are available for predicting vapor-liquid equilibrium, the applicability of these methods is subject to many restrictions. A single comprehensive and general theory is still to be developed. Thus, experimental programs are necessary to provide data for systems of academic and industrial importance and to contribute towards the development of a general theory.

Non-hydrocarbons such as nitrogen, hydrogen sulphide and carbon dioxide are frequently found in large amounts in petroleum reservoirs. Most of the methods for predicting vapor-liquid equilibria are not suitable for use when these

non-hydrocarbons are present. Many such hydrocarbon-non-hydrocarbon systems have been studied but still there is ample scope for further work. While binary systems of carbon dioxide and light hydrocarbons have been studied, only limited work has been done on systems involving carbon dioxide and hydrocarbons of higher molecular weight. For this reason, the n-hexane-carbon dioxide system was chosen for study in this work.

A variable volume windowed equilibrium cell, permitting visual observation, was used in this work. Hutton⁽¹⁶⁾ has presented a detailed description of the cell and used it for the study of gas hydrates in methane-carbon dioxide-hydrogen sulphide system.

The primary objectives of this investigation may be stated as follows.

1. To use the equipment in the study of the phase behavior of n-hexane-carbon dioxide system in the temperature range of 100 to 300°F.
2. To compare the equilibrium ratios thus obtained with values reported in the literature on related systems.
3. To see whether this information could be used in conjunction with data on other paraffin hydrocarbon systems containing carbon dioxide to improve the prediction of K-ratios in carbon dioxide-paraffin hydrocarbon systems.

II. THEORY

A. The Criteria of Equilibrium

Equilibrium in a closed system implies a situation in which there is no change with respect to time. In thermodynamics, where attention is focused upon a particular quantity of material, this implies no change in the properties of that material with time. Actually a true state of equilibrium is probably never reached, however, the rate of change becomes very slow as equilibrium is approached. Equilibrium is assumed in scientific studies when changes can no longer be detected with the available measuring devices.

Gibbs⁽¹²⁾ showed that a multiphase system at constant temperature and pressure will be at equilibrium, if the chemical potential, μ , has the same value for a given component in each phase. He defined the chemical potential of a component in a mixture as

$$\mu_i = \left| \frac{\partial G}{\partial N_j} \right|_{P,T, i=1,n} \quad (1)$$

$i \neq j$

Hence, the chemical potential of any component in a phase is the rate at which the total free energy of that phase changes as one changes the amount of that particular component, keeping the pressure, temperature, and amounts of all the other components of the phase the same.

Mathematically, Gibbs⁽¹²⁾ showed that the necessary and sufficient condition for equilibrium to exist in a system at constant temperature and pressure is

$$dG = 0 \quad (2)$$

For design calculations, equilibrium between the vapor and liquid phases in contact is assumed in natural gas-condensate wells and in many types of commercial equipment such as fractionating columns and absorbers.

B. Equilibrium Ratio

Souders, Selheimer, and Brown⁽⁴²⁾ proposed the concept of 'equilibrium constants'. They defined the equilibrium constant, K , as the ratio of the mole fraction of a component in the vapor phase, y , to the mole fraction of the same component in the liquid phase, x , at the temperature and pressure of equilibrium. Hence, for a component, i ,

$$K_i = \frac{y_i}{x_i} \quad (3)$$

The term 'equilibrium constant' is misleading because equilibrium constants are functions of temperature, pressure and composition of the system. Musket⁽²⁶⁾ has suggested the term 'equilibrium ratio' usually written as K-ratio, K-factor or K-value.

A knowledge of equilibrium ratios for each component in a mixture is essential for making vapor-liquid equilibrium calculations. Consequently, many methods have been proposed for correlating these ratios in terms of the temperature, pressure, and composition of the mixture. These methods, however, are subject to many restrictions and are frequently only applicable to specific systems under given conditions of temperature and pressure. A review of these techniques is presented here.

C. Ideal Equilibrium Ratios

If the molecules of the components of the solution are similar in nature and size so that the intermolecular forces between like and unlike molecules are the same and if the components mix without the complicating effects of chemical combination or molecular association, the solution would obey Raoult's Law.

$$p_i = x_i p_i^V \quad (4)$$

where, p_i is the partial pressure of the i^{th} component of the solution and p_i^V , the vapor pressure of the i^{th} component in its pure state at the temperature of equilibrium.

If a gas mixture behaves according to the ideal gas Law, then Dalton's Law states that the total pressure of a gas is equal to the sum of the partial pressures of the components present. Thus:

$$p_i = Y_i p \quad (5)$$

where p is the total pressure of the system.

The equilibrium ratio, K_i , from equations (4) and (5) becomes

$$K_i = \frac{Y_i}{x_i} = \frac{p_i^V}{p} \quad (6)$$

Thus, for any two phase system where Raoult's Law and Dalton's Law are applicable to liquid and vapor phases respectively, the equilibrium ratio can be obtained for any component as long as the vapor pressure of that component is known at the necessary temperature.

Equation (6) indicates a useful method of representing K-ratios graphically. On taking logarithms of both sides, one obtains,

$$\log K_i = \log p_i^V - \log p \quad (7)$$

Therefore, a log-log plot of K_i versus p will give a straight line of slope -1, passing through $K_i = 1.0$ where $p = p_i^V$ at the temperature in question.

Generally speaking K-values predicted by this method are restricted to low pressures and to ideal solutions. At higher pressure, particularly close to critical, severe deviations from actual K-values will occur. The reasons for these deviations are that Raoult's and Dalton's Laws are not exact even in relatively simple mixtures of hydrocarbons at higher pressures. Normal pentane and heavier n-paraffin hydrocarbons conform to these ideal Laws over limited ranges of pressure and temperature, but the presence of components such as water, nitrogen, hydrogen, hydrogen sulphide, carbon dioxide, and olefins may frequently cause deviations from these laws.

D. Ideal Solution Equilibrium Ratios

Even though, at low pressures, solutions may be assumed to behave ideally, departure from ideal gas behavior at elevated pressures will cause a discrepancy between ideal K-ratios and actual K-ratios. Lewis⁽²⁴⁾ suggested the use of fugacity instead of pressure whenever the fluids behave non-ideally. Thus, if partial pressures and pressures are replaced by fugacities, a closer approximation to actual K-values can be obtained.

An ideal solution may be defined as one in which the fugacity of each component is proportional to its mole fraction. Equilibrium ratios defined in terms of fugacities are usually called 'ideal solution equilibrium ratios'.

Fugacity, at constant temperature, T, is defined as:

$$dG = R T d \ln f = V d P \quad (8)$$

where, f is the fugacity, V, the molal volume of the component, and P, the system pressure.

For the vapor phase, the Dalton's Law type equation becomes:

$$\bar{f}_i^V = y_i f_i^L \quad (9)$$

and for the liquid phase the Raoult's Law type equation becomes:

$$\bar{f}_i^L = x_i f_i^L \quad (10)$$

where, f_i^V and f_i^L are the fugacities of a component i as a vapor and liquid respectively at the pressure and temperature of equilibrium, the bar denotes the fugacity of a component in the mixture. At equilibrium;

$$\bar{f}_i^V = \bar{f}_i^L \quad (11)$$

Thus the K-factor becomes

$$K_{is} = \frac{y_i}{x_i} = \frac{f_i^L}{f_i^V} \quad (12)$$

K_{is} is a function of system temperature and pressure only. The use of fugacities is useful in predicting K-factors for many systems over a wider range of pressures and temperatures, but the concept breaks down for all systems as the critical conditions are approached.

E. Convergence Pressure Concept

Basically, it is recognized that the equilibrium ratios for any component are functions of the temperature, pressure and composition of the system. Attempts have been made to suggest a suitable means for correlating the effect of composition. This has resulted in the concept of convergence pressure which is based upon the fact that the K-factors are observed to converge to unity at some pressure for each temperature chosen.

The convergence pressure may be defined as the pressure at which equilibrium ratios for all components appear to converge to unity at the system temperature. The K-values are continuous to this pressure, if the equilibrium temperature is critical temperature of the system. At any other temperature K-values, when plotted on a log K vs log P plot, appear to converge to unity.

One may assume that the equilibrium ratio may be expressed as a function of temperature, pressure and composition as follows:

$$K = \phi (P, T, x_1, x_2 \dots x_n) \quad (13)$$

where, n is the total number of components present. From Gibbs' phase rule, for two phase equilibria, the total number of independent variables is equal to the number of components. Thus, number of independent variable used to correlate K -values may be expressed as:

$$K = \phi'(P, T, x_1, x_2, \dots x_{n-2}) \quad (14)$$

if we express,

$$K = \phi''(P, P_{CV}) \quad (15)$$

then,

$$P_{CV} = \phi'''(T, x_1, x_2, \dots x_{n-2}) \quad (16)$$

where, P_{CV} is the convergence pressure of the system. From equation (16) it follows that for a binary system convergence pressure is independent of composition and depends upon temperature alone. It has been shown⁽¹³⁾ that at temperatures intermediate to the critical temperatures of the two components the convergence pressure of any binary mixture is equal to the critical pressure of the mixture with critical temperature the given temperature.

For a two phase ternary system, application of Gibbs' phase rule indicates that three variables must be fixed in order to completely determine the system. Carter, Sage, and Lacey⁽⁶⁾ defined the composition parameter C_2 as follows.

$$C_2 = \frac{x_2}{x_2 + x_3} \quad (17)$$

Where the components are numbered in the order of decreasing volatility. Hadden⁽¹⁴⁾ has suggested the use of a composition parameter based on mass fractions, rather than mole fractions, defined by:

$$M_2 = \frac{m_2}{m_2 + m_3} \quad (18)$$

Most methods of calculating convergence pressure in ternary system are based on these composition parameters. A ternary mixture is reduced to an equivalent binary composed of component 1 and the pseudo heavy component $\bar{2}$ made of components 2 and 3. A knowledge of the composition parameter M_2 is used in establishing the critical temperature $t_{c\bar{2}}$ of the hypothetical component. The concept of an equivalent binary is extended to multi-component systems. For each component that is added to a mixture after the second one, a composition parameter is fixed. For example, for a quaternary system, the convergence pressure is determined by fixing the system temperature and two composition parameters M_2 and M_3 . The lightest component of the quaternary mixture is taken as the light component of the equivalent binary. Determination of the 'pseudo heavy' component of the equivalent binary mixture is now a two step process. First, components 3 and 4 are combined to give a component $\bar{3}$. This is combined with component 2 to give the 'pseudo heavy' component $\bar{2}$.

The convergence pressure concept postulates that the $\log P$ vs $\log K$ for a component in a multi-component system depends only as the system temperature and the convergence pressure

of the system. For a ternary system M_2 fixes t_{c2} and this value of the critical temperature of hypothetical heavy component determines the convergence pressure of the system.

Thus:

$$K_i = \phi(P, T, M_2) = \phi(P, T, t_{c2}) = \phi(P, T, P_{CV}) \quad (19)$$

For each M_2 there is one and only one convergence pressure and consequently, one and only one $\log P$ vs $\log K$ plot exists for each component. Hence, for a ternary system the basic postulate is in accordance with Gibbs' phase rule without any assumption. However, this is not the case for multi-component mixtures that contain more than three components. For a quaternary system, Gibbs' phase rule indicates:

$$K = \phi(P, T, M_2, M_3) \quad (20)$$

If for each distinguishable pair of values of M_2 and M_3 , there were a unique value of convergence pressure then no assumptions would be involved. However, this is not the case and many set of values of M_2 and M_3 exist to give the same convergence pressure for the system.

In general, for each set of values of M_2 and M_3 a $\log K$ vs $\log P$ isotherm exists for a given system temperature. It is assumed in this concept that for each pair of values of M_2 and M_3 that give the same value of convergence pressure, one and only one $\log K$ vs $\log P$ plot exist for each component at a given system temperature.

Many correlations^(4, 15, 27, 52) have been developed which are based on convergence pressure concept which present charts to obtain the equilibrium ratios from a knowledge of convergence pressure.

Convergence pressure has been found to be a satisfactory parameter to account for the effect of composition in paraffin hydrocarbon mixtures. However, the presence of non-hydrocarbons such as nitrogen, hydrogen, carbon dioxide, hydrogen sulphide, and water may limit the usefulness of the convergence pressure type correlations.

F. Activity Coefficients

The Lewis and Randall rule states that the fugacity of a component in an ideal solution is equal to the mole fraction times the fugacity of the pure component, evaluated at the same pressure and temperature and in the same kind of phase.

The deviations from ideal solution behavior can be taken into account by incorporating a correction factor γ into equation (10). The purpose of γ , the activity coefficient, is to account for the departure of the liquid phase from ideal solution behavior. Thus,

$$\bar{f}_i^L = \gamma_i^L x_i f_i^L \quad (21)$$

Where, γ_i^L is the activity coefficient of the i^{th} component in the liquid phase. In a similar way one can define the activity coefficient for vapor phase. Thus:

$$\bar{f}_i^V = \gamma_i^V y_i f_i^V \quad (22)$$

The activity coefficients are functions of phase composition and system temperature. For an ideal solution, they become unity.

Activity coefficients have been used for correlating data on vapor-liquid equilibria, for example, Smith and Watson⁽⁴¹⁾ have used activity coefficients to correlate the data on paraffin hydrocarbons.

Many methods have been suggested in the literature for predicting the activity coefficients from a minimum of experimental data^(3, 25, 34, 38, 39, 44, 45). These methods are based on solutions of the Gibbs-Duhem equation expressed in terms of activity coefficients. Some of these are the well known equations derived by Van Laar^(44, 45), Margules⁽²⁵⁾ and Scatchard and Hamer⁽³⁹⁾.

Vapor-liquid equilibrium data for non-ideal systems can be predicted by these equations, if constants to be used in them are known. For non-associating solutions, these equations have been used with considerable success^(2, 3, 5, 7, 10, 11, 25, 39, 40, 44, 45). Van Laar type equations are generally unsatisfactory for associating solutions. Similarly, Margules equation with two coefficients fail for associating systems and binary systems with unsymmetrical activity coefficients for the two components. In such cases, the Van Laar equation gives better results. If better results are to be expected from Margules equation, more than two constants should be used. The Scatchard and Hamer equation has been used with some success, but accurate data

on boiling points as a function of composition at constant pressure are required.

Equations of the Margules and Van Laar types have been developed for ternary systems⁽⁴⁸⁾. The objective of these proposals is to allow the prediction of the activity coefficients in such systems from data on the three possible binary combinations. However, at least some ternary information appears necessary, if reasonably accurate results are to be obtained.

There is a serious limitation on the use of these equations. They have been found to be useful in predicting vapor-liquid equilibrium data for systems containing components which are all condensable at the system temperature. They have not been used for systems containing non-hydrocarbons such as carbon dioxide and hydrogen sulphide.

III. REVIEW OF PREVIOUS EXPERIMENTAL STUDIES

The published literature gives ample evidence of the work which has been done on pure carbon dioxide and n-hexane. For example, Cramer⁽⁸⁾ has compiled the phase diagrams for carbon dioxide up to 12,000 atmospheres for temperatures ranging from -100°C to 200°C and for pressures up to 220 atmospheres for temperatures up to 1000°C . Sweigert, Weber, and Allen⁽⁴³⁾ have reported thermodynamic properties of carbon dioxide. The properties of n-hexane at atmospheric pressure have been studied in detail and were summarized by Rossini⁽³⁶⁾. The pressure-volume-temperature relations of n-hexane have been studied by Kelso and Felsing^(18, 19) at pressures up to 4500 psia.

Kuenen^(20, 21, 22) was perhaps the first to study the behaviour of paraffin hydrocarbons and carbon dioxide mixtures. His study indicated a minimum boiling azeotropic behavior for the binary carbon dioxide-ethane system.

Donnelly and Katz⁽⁹⁾ have reported the solid-liquid-vapor equilibrium data for the methane-carbon dioxide system in the temperature range -100 to 29°F and for pressures up to 1150 psia. Their study showed that the carbon dioxide-methane system exhibits a normal critical locus and vapor-liquid equilibria down to the triple point of carbon dioxide.

Poettmann and Katz⁽²⁹⁾ studied the phase behavior of mixtures of carbon dioxide with propane, butane, and pentane. They have presented complete pressure-temperature diagrams

for the three binaries and pressure-composition diagram at four temperatures. Their study indicated a sharp downward curvature of the critical locus at the carbon dioxide end of the curve for the propane-carbon dioxide system, thereby indicating that the forces tending to form a minimum boiling azeotrope as in the ethane-carbon dioxide system had not yet completely disappeared. The systems butane-carbon dioxide and pentane-carbon dioxide behaved normally.

Akers, Kelley and Lipscomb⁽¹⁾ studied the propane-carbon dioxide system and provided data at lower temperatures between -40° and 32°F and for pressures up to 507 psia. They presented a chart for predicting equilibrium ratios for carbon dioxide for a convergence pressure of 1000 psia. Reamer, Sage and Lacey⁽³²⁾ studied the propane-carbon dioxide system at higher temperatures and presented vapor-liquid equilibria data at temperatures ranging from 40° to 160°F and for pressures up to 1000 psia. They confirmed the finding of Poettmann and Katz⁽²⁹⁾ that the azeotrope forming tendencies in this system existed. Akers, Kelley and Lipscomb⁽¹⁾ from their study on this system at lower temperatures concluded that the azeotrope forming tendency increases as the temperature decreases. Roof and Baron⁽³⁵⁾ have determined the binary critical locus for propane-carbon dioxide system. Their results are in considerable disagreement with the results of previous studies^(29, 32) on this system.

Olds, Reamer, Sage and Lacey⁽²⁸⁾ studied the butane-carbon dioxide system and presented vapor-liquid equilibria data at temperatures ranging from 100° to 280°F and pressures up to 1184 psia. Their results are in fair agreement with those of Poettmann and Katz⁽²⁹⁾.

Reamer and Sage⁽³³⁾ have presented data on vapor-liquid equilibrium for the n-decane-carbon dioxide system for temperatures ranging from 40° to 460°F and for pressures up to 2500 psia. The behavior of the system was similar to that encountered in other binary systems containing a hydrocarbon with carbon dioxide.

A few multicomponent systems of carbon dioxide with hydrocarbons have been studied. Poettmann and Katz⁽³⁰⁾ have studied a carbon dioxide-natural gas condensate system at temperatures ranging from 100° to 250°F and for pressures up to 2900 psia. They also presented charts for predicting the equilibrium ratio values for 0 to 10 mole percent carbon dioxide in natural gas distillate and similar systems. From this and their previous study of the binary carbon dioxide systems⁽²⁹⁾ they concluded that the lower the molecular weight of the hydrocarbon with which the carbon dioxide is mixed, the greater will be the deviation of the equilibrium constant for carbon dioxide from the ideal behavior.

Poettmann and Katz⁽³¹⁾ also studied the vaporization characteristics of carbon dioxide in a natural gas-crude oil system and presented data for pressures from 600 to 8500 psia and temperatures ranging from 38° to 202°F. They found that

the variation of carbon dioxide concentration up to 12 mole percent in the composite mixture did not affect the equilibrium ratio value of the hydrocarbon constituent or the K-value of carbon dioxide itself.

Jacoby and Rzasa⁽¹⁷⁾ reported data on the equilibrium ratio of carbon dioxide in a natural gas condensate system for pressures up to 4000 psia and a temperature interval of 100° and 200°F. Their mixtures were quite similar to those studied by Poettmann and Katz⁽³⁰⁾ except for the non-hydrocarbons hydrogen sulphide and nitrogen. The equilibrium ratios for carbon dioxide compare well with those of Poettmann and Katz.

Saxena and Robinson⁽³⁷⁾ studied the methane-carbon dioxide-butane system over a temperature range of -20°F to 100°F and for pressures from 400 to 1200 psia. Their study indicated that the equilibrium ratios for butane are somewhat higher than those predicted by NGPSA⁽²⁷⁾. They have also reported some inconsistencies in the data of Wang and McKetta⁽⁴⁶⁾ who studied this system between -140° and 100°F in the pressure range of 400 to 1700 psia.

IV. EXPERIMENTAL STUDIES

A. Experimental Apparatus

The equipment used in this work has been described in detail by Hutton⁽¹⁶⁾. Essentially, it consisted of a windowed equilibrium cell whose volume could be varied by adding or withdrawing mercury by means of a Ruska mercury displacement pump.

The equipment in its existing state could not be used for temperatures higher than 125°F, because of the lucite jacket surrounding the cell and the temperature controlling fluid, varsol. Both were unsuitable for temperatures above 150°F.

In order to overcome these difficulties, the equilibrium cell was mounted inside a windowed steel-jacket in such a way that the contents of cell could be viewed by lighting the jacket window. The glass used in the jacket window was identical to one used in the equilibrium cell window. The jacket was insulated with asbestos. Varsol was replaced by primol-D, well suited for temperatures up to 300°F. A gear-pump was used for circulation of primol-D through the steel-jacket surrounding the equilibrium cell, the existing centrifugal pump being inadequate to provide the required head with primol-D. The total power of the temperature bath was increased from 1500 watts to 3000 watts by replacing the 500 watt immersion heater by one rated at 2000 watts. Figure 1 indicates the schematic diagram of the equipment.

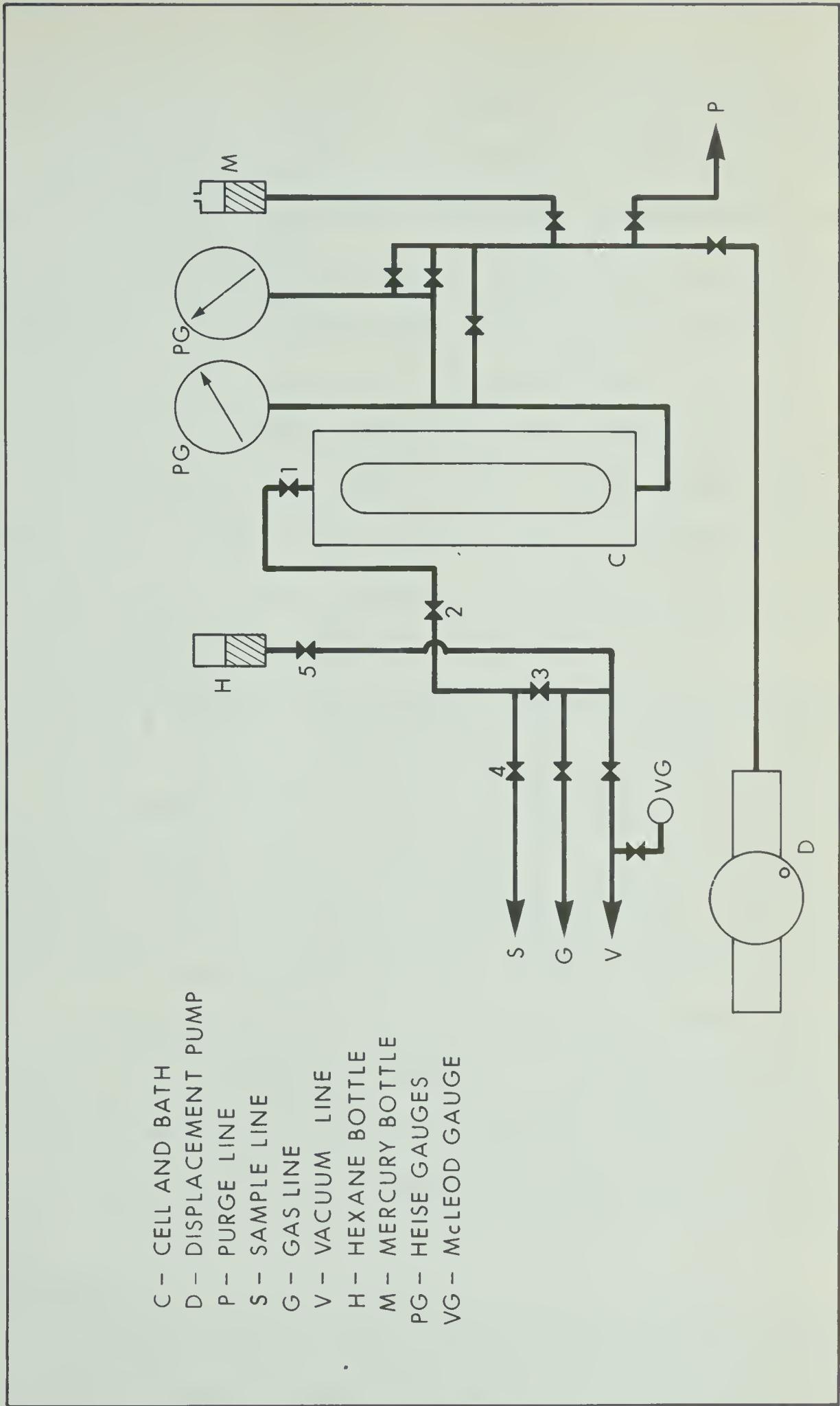


FIG.1 SCHEMATIC DIAGRAM OF EQUIPMENT

Temperature was measured by means of an iron-constantan thermocouple inserted into the side of the equilibrium cell. The thermocouple was calibrated against a standard precision mercury thermometer accurate to 0.1°C and readable at 0.05°C . A Leeds and Northrup model 8686 millivolt potentiometer was used for measuring the potential. During the course of each run temperature fluctuations were controlled to within $\pm 0.5^{\circ}\text{F}$, and temperatures were read to within $\pm 0.1^{\circ}\text{F}$.

Pressure was measured using two Heise Bourdon tube gauges rated at 5000 lbs/in^2 and 1000 lbs/in^2 . Both gauges were calibrated with a Ruska dead weight tester. Readings on the 5000 lbs/in^2 were made to within $\pm 3 \text{ lbs/in}^2$ and on the 1000 lbs/in^2 to within $\pm 1 \text{ lb/in}^2$.

Volume measurements were made by means of a cathetometer provided with a vernier scale and capable of reading within 0.05 mm . The equilibrium cell was calibrated for its volume versus cathetometer reading by adding 1.5 c.c. of mercury each time by the Ruska mercury displacement pump. The calibration of the displacement pump was checked within an accuracy of 0.05 c.c. by displacing 1.5 c.c. of mercury each time and collecting it in a graduated burette. Volume corrections due to meniscus effects were small and could be neglected in most cases. The details of such calculations are shown in the appendix.

B. Materials

The materials used in this investigation were sufficiently pure so that no further treatment was considered necessary. The n-hexane was research grade product from Phillips

Petroleum Company with a minimum purity of 99.95 mole percent. The carbon dioxide was supplied by Canadian Liquid Air Company and it had a purity of 99.9 percent. No detectable impurity was found when a sample of each pure component was run through gas chromatograph.

C. Experimental Procedure

The equilibrium cell was first cleaned several times using liquid butane and alcohol as solvents. The entire system was evacuated and pressure tested with mercury to a pressure of 4000 lbs/in² and then with nitrogen to the same pressure.

The cell was purged with carbon dioxide and evacuated. This procedure was repeated three times. Hexane was then introduced into the evacuating system from a hexane bottle by opening valve 5. The cell was again evacuated. Hexane was again introduced into the cell and was partially allowed to boil off. Carbon dioxide was introduced into the cell at high pressure from the gas cylinder. The cell valve was then closed.

The experiments were conducted at a series of constant temperatures. The bubble point was observed by the disappearance of the last drop of vapor. It was usually possible to reduce the vapor phase to a volume of about 1 cu. mm. except near the critical region.

The amount of liquid and vapor phases were measured by reducing pressure from the bubble point in small intervals. Care was taken to keep the cell in a perfectly vertical

position with the help of a pointer before making volume measurements. The equilibrium cell was rocked through an angle of approximately 180° several times to ensure equilibrium before taking readings of pressure and temperature and measuring the amount of each phase. Equilibrium was assumed when there was no change in pressure and temperature on further rocking of the cell.

The dew point was noted by the first appearance of liquid drops on the cell window glass. The cell window, just above the mercury surface, usually appeared to be a little moist at the dew point. In some cases, it was not possible to reduce the pressure to the dew point, because of limited volume of the equilibrium cell. In such cases, dew point measurements were made after a sample was withdrawn for analysis. However, in some cases, when a greater percentage of hexane was present and at lower temperatures, dew points were obtained by extrapolation of the plot of percent liquid versus pressure. It was rather difficult to visually determine the exact dew points, particularly when the carbon dioxide concentration in the mixture was high. In this region, the dew points may be off by as much as ± 20 psi from the true value.

D. Analysis

The overall composition of the mixture under study was made by using a Burrell Corporation model K-2 gas chromatograph. A column packed with silicone-550 on celite was used for the

separation of carbon dioxide and n-hexane. A satisfactory separation was obtained under the following conditions.

Column length: 1 meter
Column temperature: 86^oF
Carrier gas: Helium at 64.3 ml/min
Detector current: 200 m.A.

The column was calibrated by adding known amounts of each pure component and obtaining the corresponding peak heights. The volume of several samplers and the volume of the manifold in which they fit were measured by displacement with mercury. Carbon dioxide was flushed into the column through these samplers. The sampler bath temperature was kept at 50^oC and the pressure was dropped to atmospheric before carbon dioxide was introduced into the column. Known amounts of n-hexane were injected into the column by means of a Hamilton micro syringe.

A mixture of known composition of carbon dioxide and hexane was made in a glass bulb provided with vacuum stop-cocks at each end and a vacuum silicone seal at the top. The bulb was evacuated and weighed. Some hexane was introduced into this evacuated bulb through the vacuum seal by means of a syringe and weighed. The bulb assembly was then connected to a carbon dioxide gas cylinder. The lines were evacuated and some carbon dioxide was taken in to the bulb by opening the stop-cock. The stop-cock was closed and the bulb assembly was weighed again. From these three weighings, the composition

of the mixture was calculated. This bulb was heated by means of the heating tape to ensure a single phase and a sample was withdrawn by means of a syringe and injected into the column. The result obtained by chromatographic analysis agreed to within 0.3 mole percent of the gravimetric analysis. Thus, the calibration based on pure components was considered adequate and is presented in Figure 19 in the appendix.

E. Sampling Technique

The mixture in the equilibrium cell was brought into a single phase by compressing above the bubble point pressure. The sample line as well as the sampling flask were evacuated. Valve 2 was closed and valve 1 was then opened keeping the pressure well above the bubble point pressure. The equilibrium cell was rocked for sufficient time to ensure equilibrium. Valves 1 and 3 were then closed. Thus, a small sample was trapped between two needle valves in high pressure autoclave stainless steel tubing. This sample was then flashed into the evacuated 1 liter sampling flask by opening valve 2. To avoid any condensation of hexane, the entire sampling line and sampling flask were kept heated by means of the heating tape and heating jacket respectively. The sample was left overnight to become uniform in composition by diffusion. A sample was withdrawn from this flask by means of a syringe and injected into the column for analysis.

V. EXPERIMENTAL RESULTS

Five mixtures of carbon dioxide and n-hexane were studied in a temperature range 100 to 300°F. Figure 2 presents pressure versus percent liquid data at a series of temperatures for a mixture containing 90.7 mole percent carbon dioxide. For this mixture, at 220°F, the amount of liquid present at any pressure was too small for accurate volumetric measurements. Thus, only the dew points were determined and consequently this isotherm is shown dotted. The pressure-temperature diagram with constant percent liquid lines for this mixture is presented in Figure 3. This figure was obtained by cross-plotting the data of Figure 2. The lines of constant percent liquid converge at a critical point of the mixture. These data, together with the data for the other mixtures, are presented in Table 1 and 2 of the appendix.

Figure 4 is the composite pressure-temperature diagram for the carbon dioxide-n-hexane system. Due to the temperature limitations of the experimental apparatus, the phase envelopes of mixtures containing less than 84.6 mole percent carbon dioxide could not be completely defined. Thus, part of the phase envelope for these mixtures is shown dotted.

The critical points for the three mixtures, containing 84.6 mole percent and higher amounts of carbon dioxide, were determined. Two additional points were obtained on the critical locus, in order to define it more adequately. These are also shown in Figure 4. The data on the critical locus

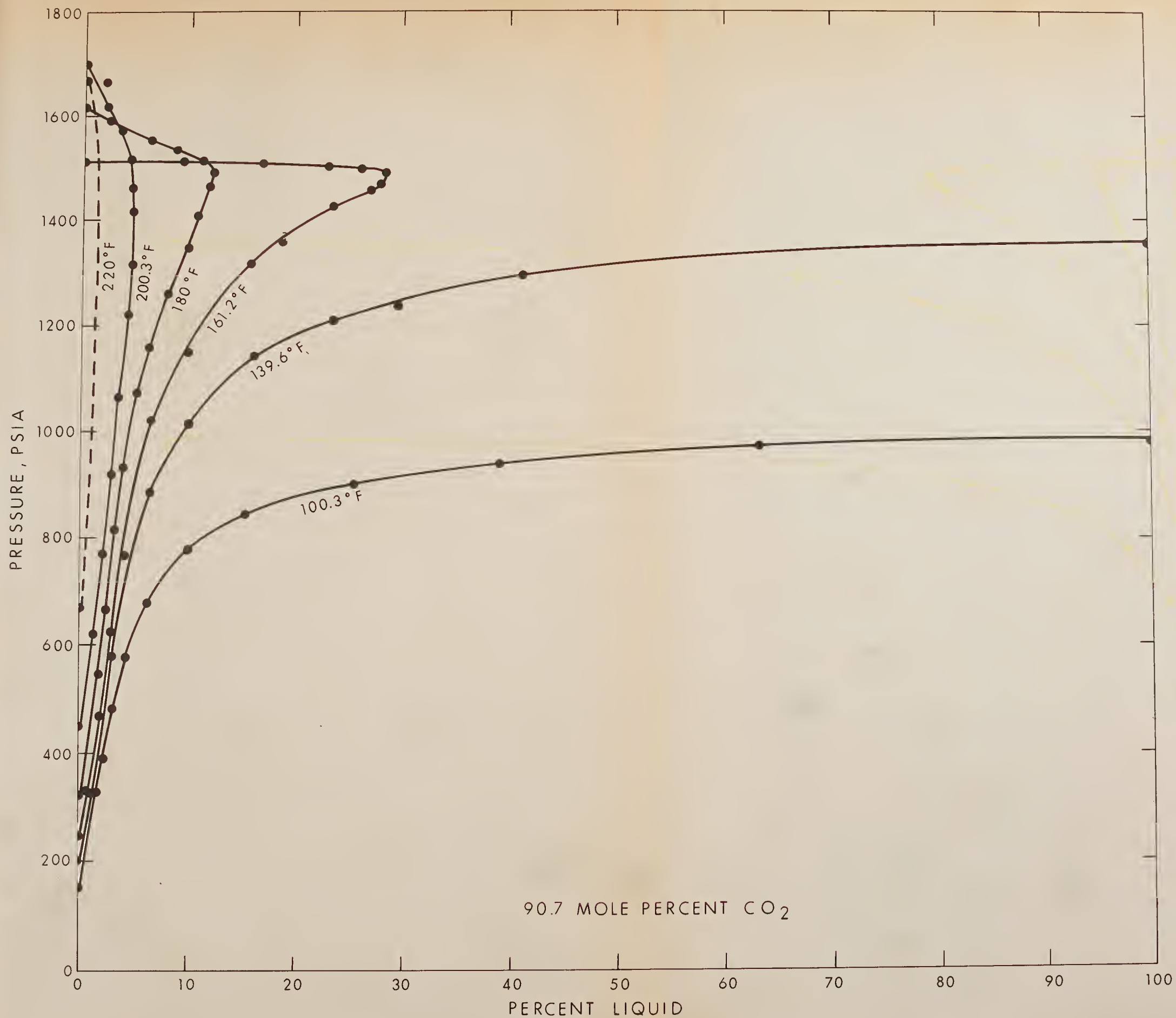


FIG. 2 PERCENT LIQUID ISOTHERMS FOR THE CO₂-n-C₆H₁₄ SYSTEM

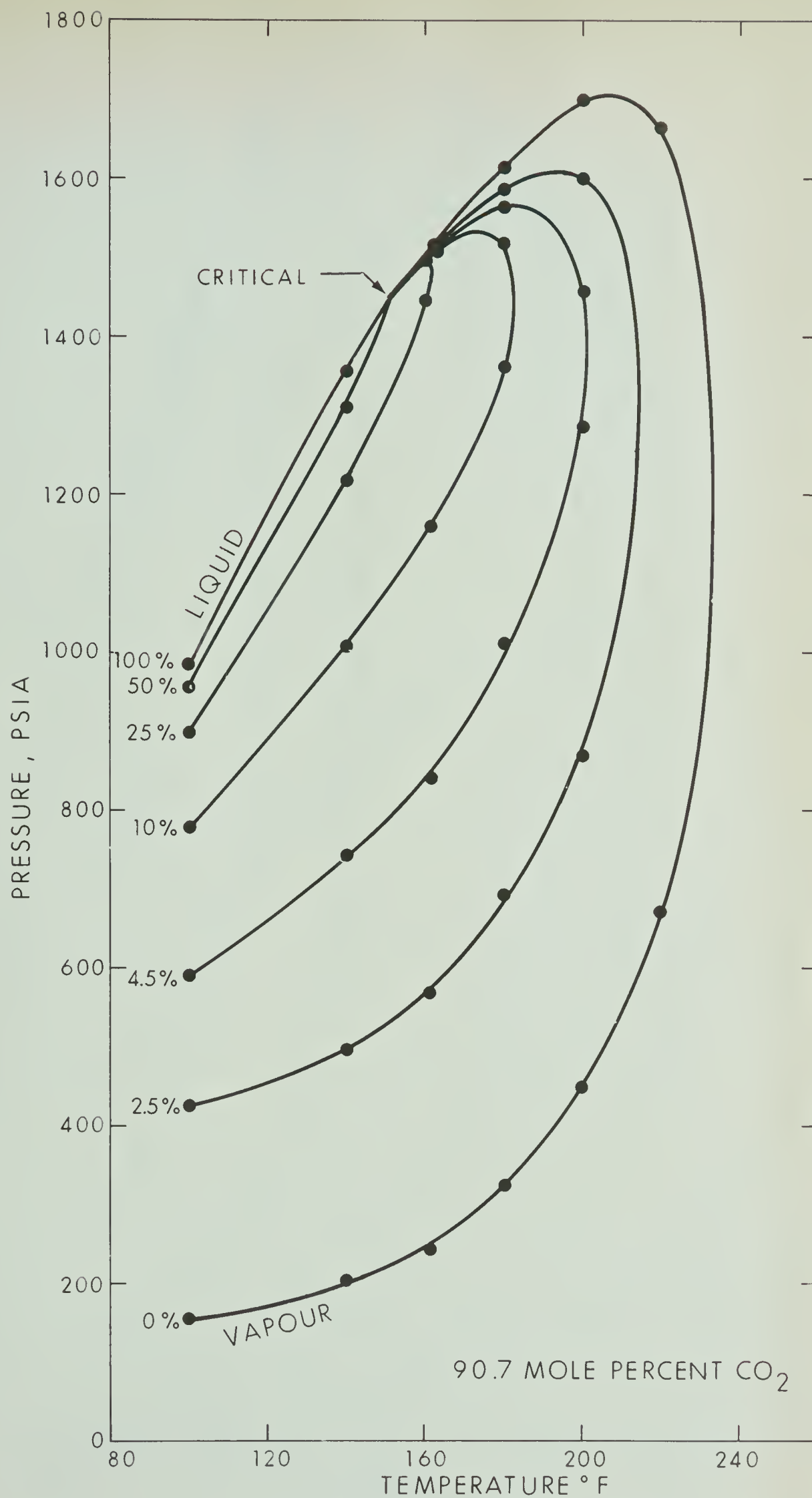


FIG.3 PHASE DIAGRAM SHOWING CONSTANT PERCENT LIQUID LINES

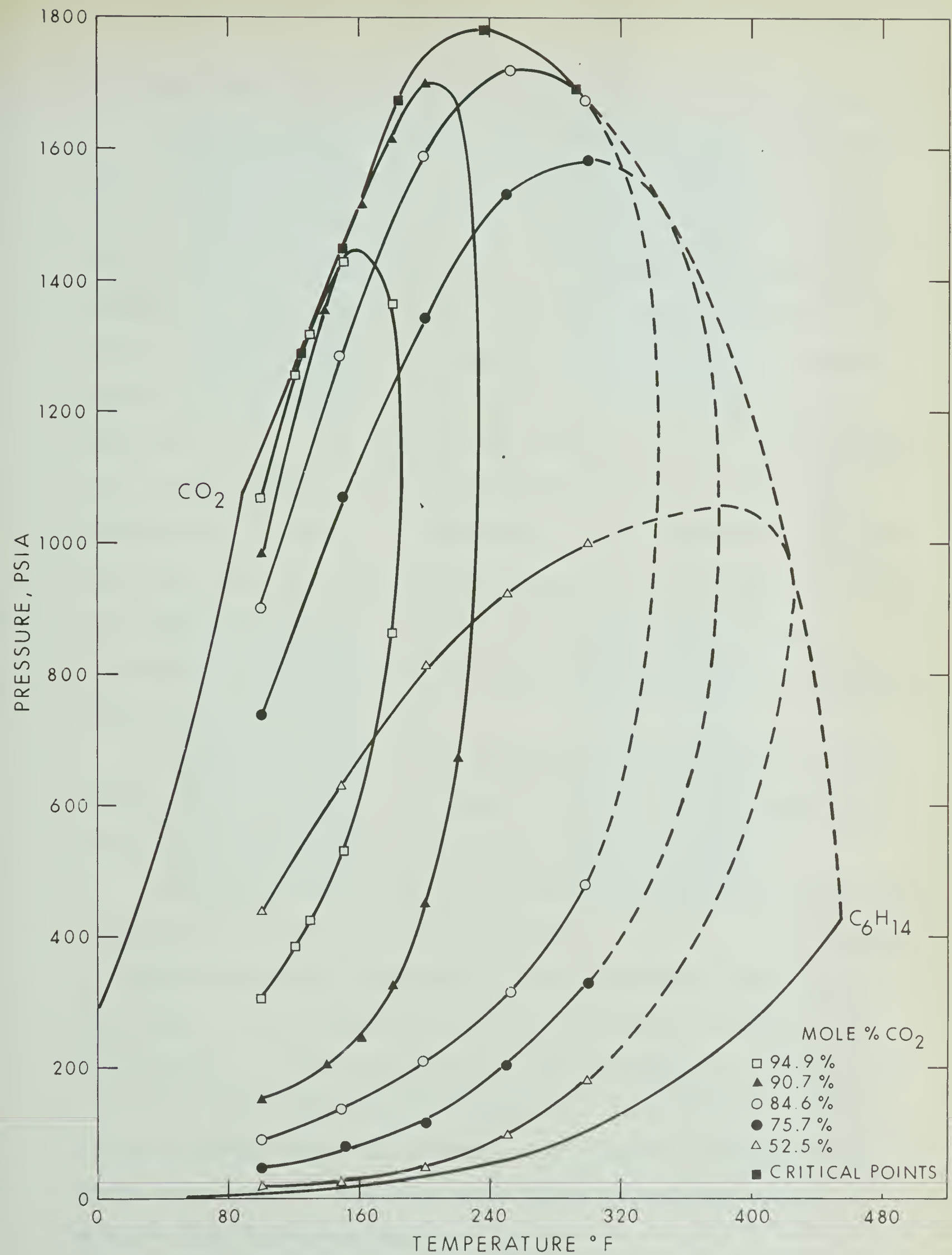


FIG.4 PRESSURE TEMPERATURE DIAGRAM FOR CO₂ -n- C₆H₁₄ SYSTEM

for this system are also presented in Table 3 of the appendix.

Figure 5 shows the photographs of the critical opalescence. The critical phenomenon in this system was marked by the exhibition of reddish-brown color in the entire mass of the mixture, when viewed in transmitted light. Photograph (a) shows this condition. When the critical conditions were maintained for a longer period of time, the reddish-brown coloration was more intense in the middle portion of the mass as can be seen in photograph (b). The sharp color change in the critical mixture by a slight change in the system pressure can be seen from photograph (c) and (d). Photograph (c) was taken at a pressure of 3 psi above the critical pressure while photograph (d) shows the condition of the mixture at 3 psi below the critical pressure. A thin meniscus had appeared at the latter conditions as seen in photograph (d).

The pressure-composition diagrams for this system at five temperatures are shown in Figures 6 to 10. These figures are obtained by cross-plotting the data shown in Figure 4.

The equilibrium ratios for n-hexane and carbon dioxide were calculated by reading the compositions of liquid and vapor phases at suitable pressure interval from the pressure-composition diagrams at each temperature and are tabulated in Table 4 of the appendix. These K-values are also presented in Figures 11 to 15 on conventional log K versus log P coordinates. These figures further show the K-values for n-hexane obtained from NGPSA data book⁽²⁷⁾ together with those calculated using Dalton's and Raoult's Laws.



(a)



(b)



(c)



(d)

Figure 5. Critical Opalescence in the Carbon Dioxide-n-Hexane System

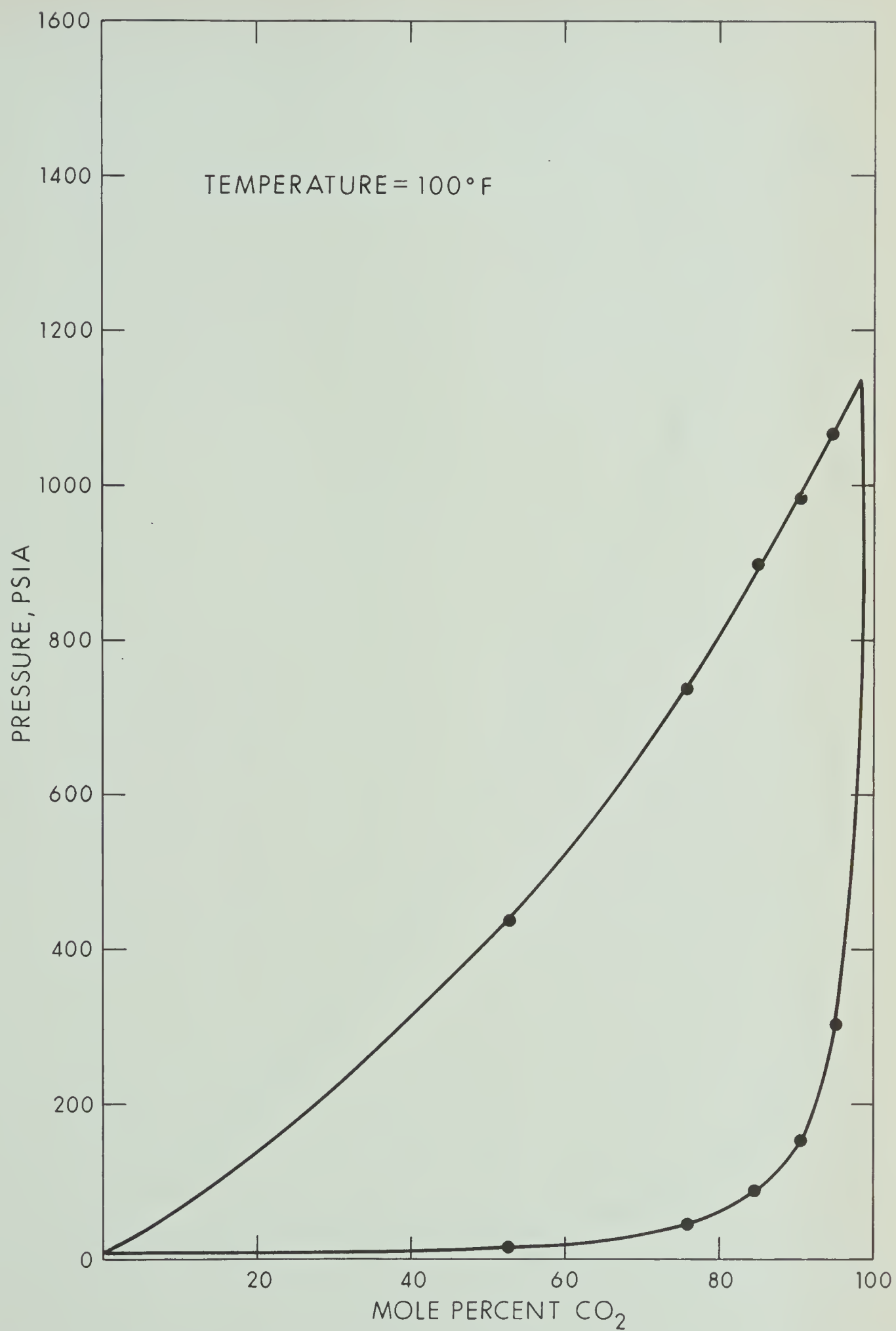


FIG.6 PRESSURE COMPOSITION DIAGRAM FOR CO₂-n-C₆H₁₄ SYSTEM

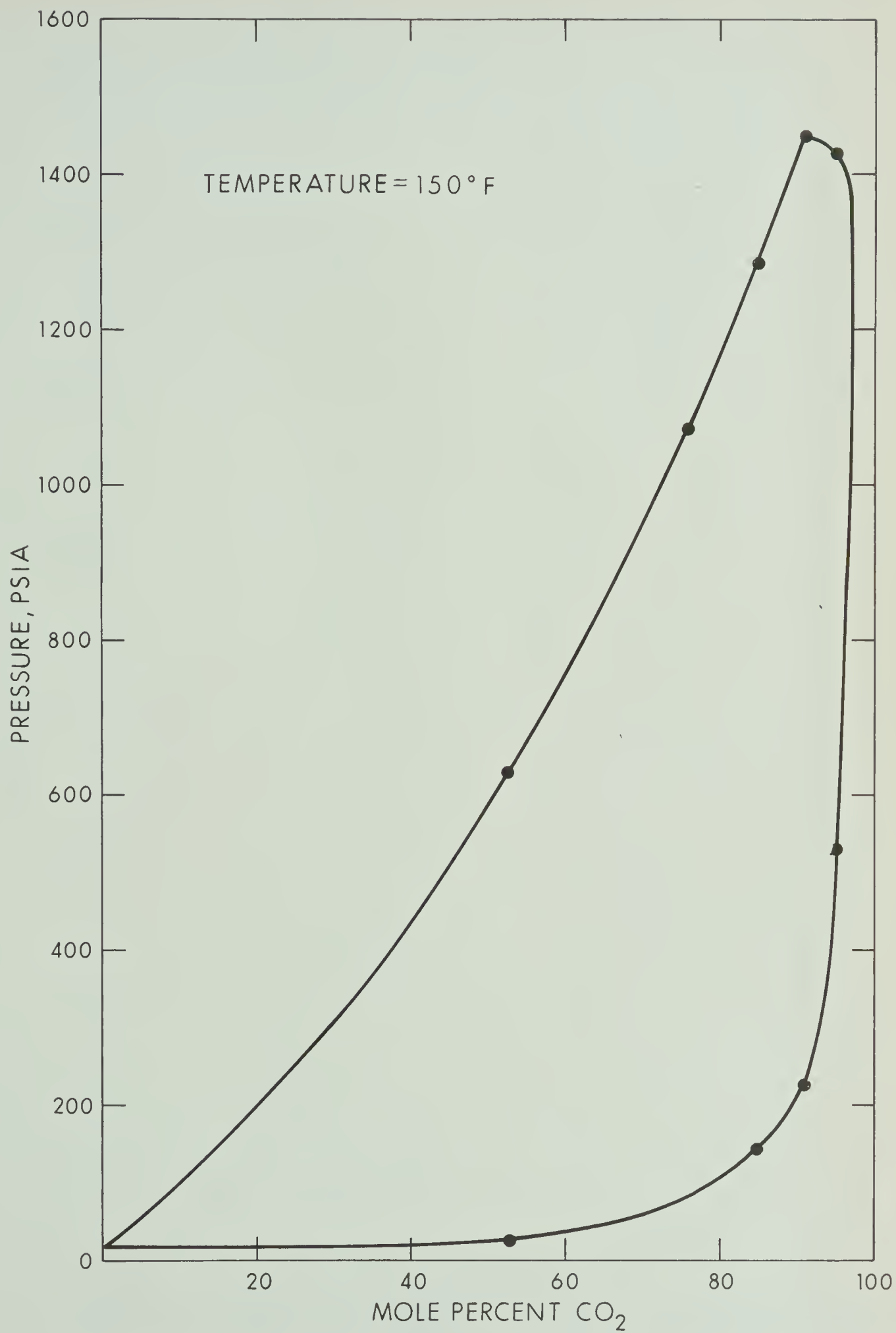


FIG.7 PRESSURE COMPOSITION DIAGRAM FOR CO₂-n-C₆H₁₄ SYSTEM

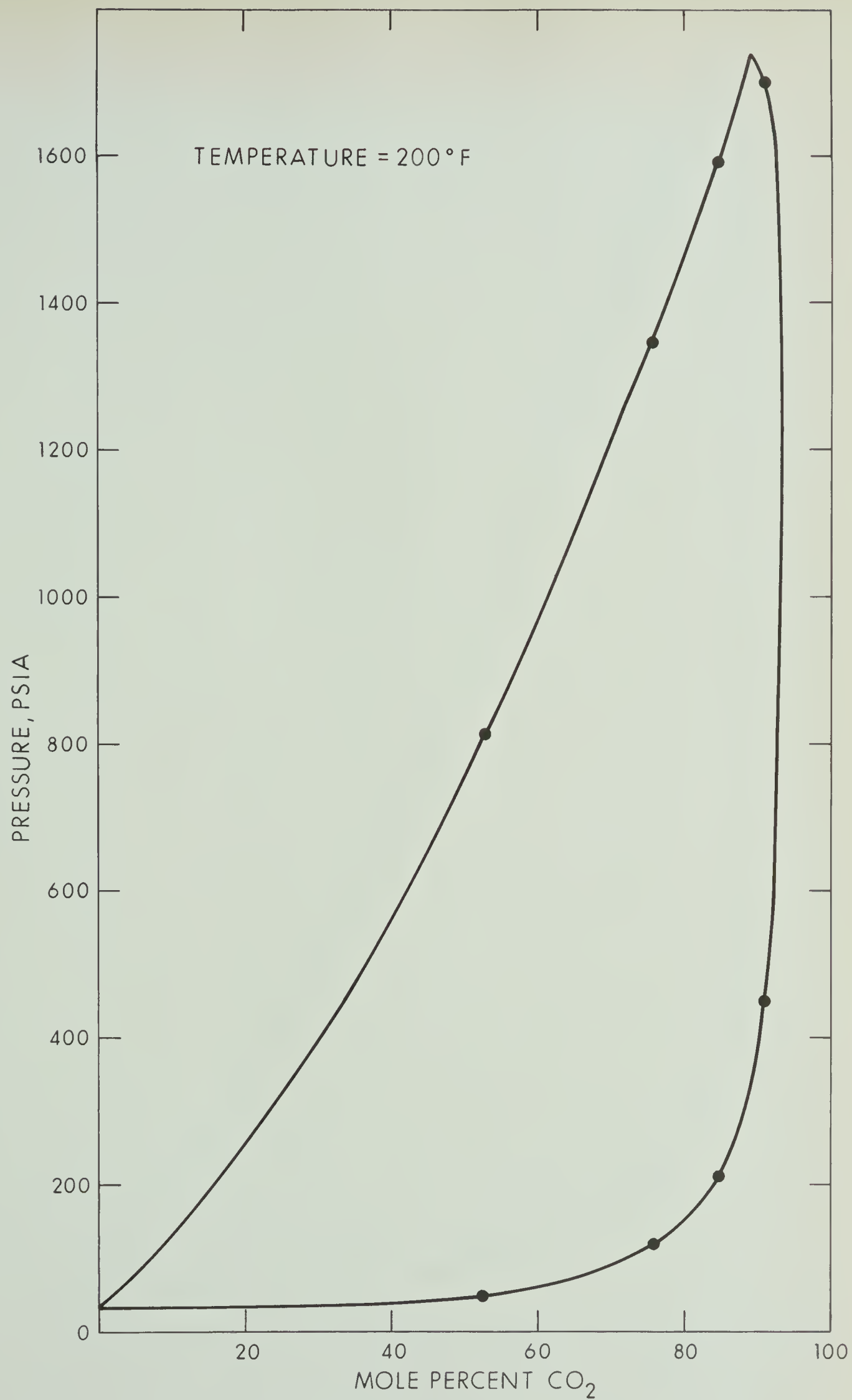


FIG.8 PRESSURE COMPOSITION DIAGRAM FOR CO₂-n-C₆H₁₄ SYSTEM

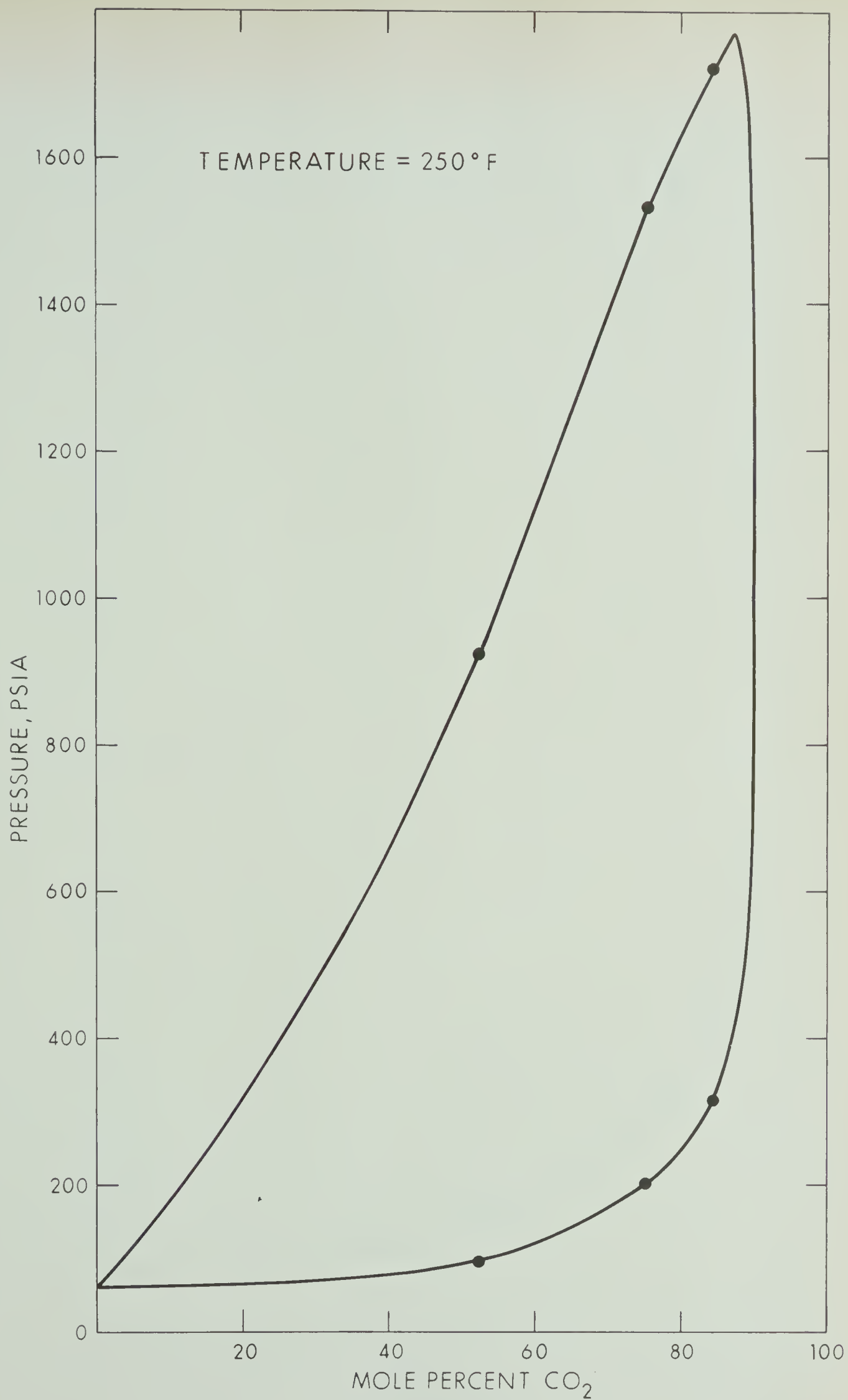


FIG. 9 PRESSURE COMPOSITION DIAGRAM FOR CO₂-n-C₆H₁₄ SYSTEM

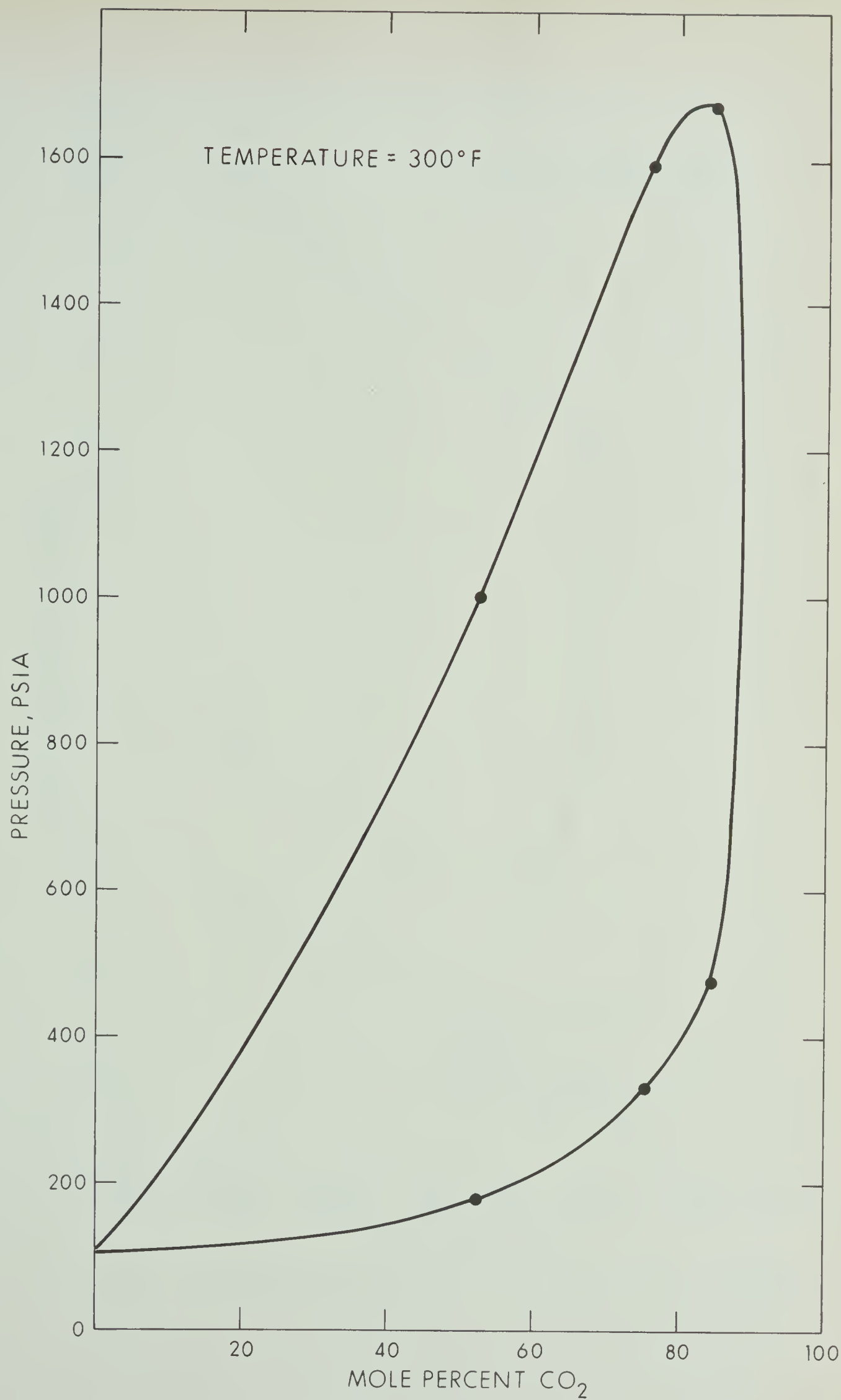


FIG.10 PRESSURE COMPOSITION DIAGRAM FOR CO₂-n-C₆H₁₄ SYSTEM

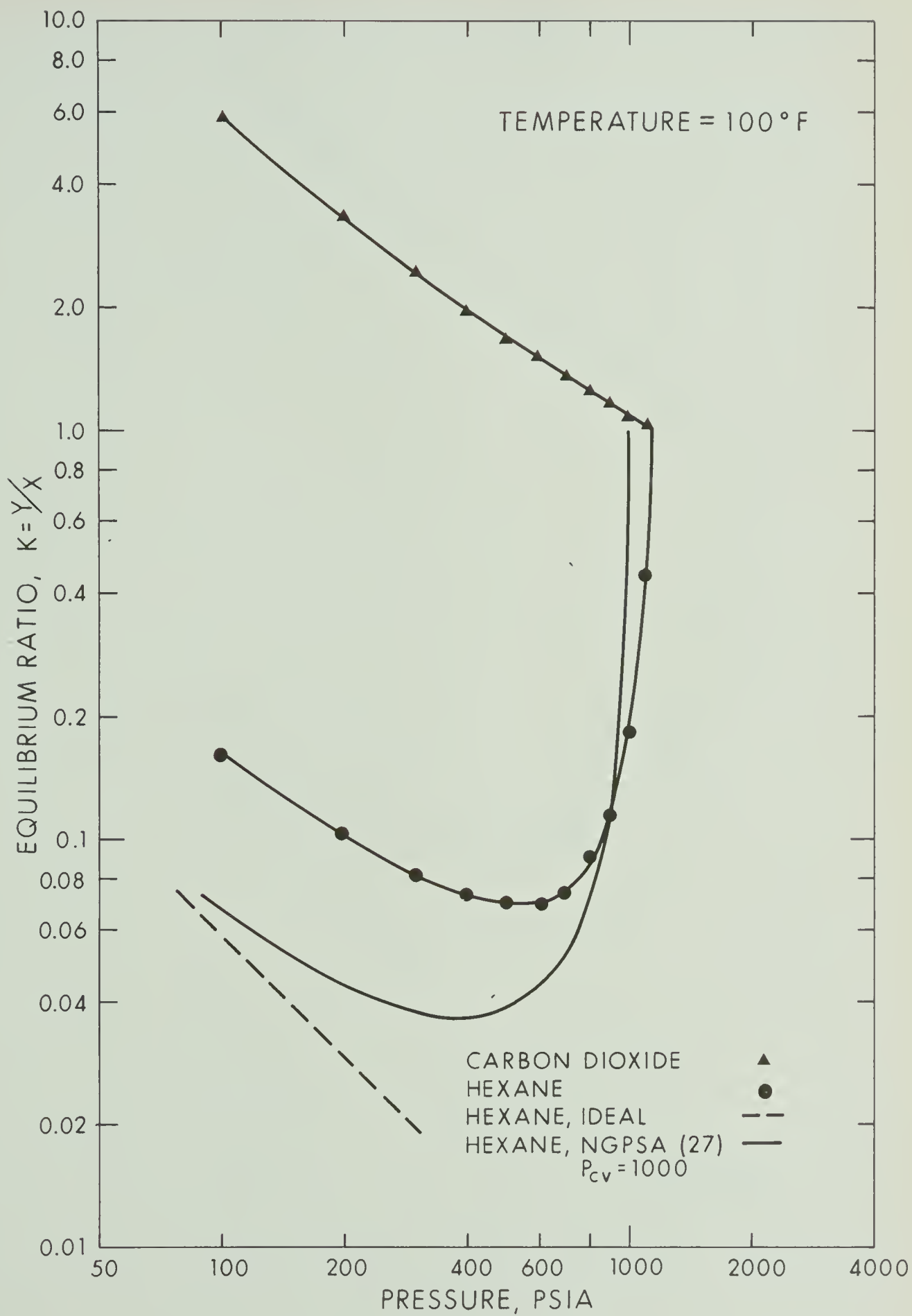


FIG.11 EQUILIBRIUM RATIOS FOR CO_2 - n - C_6H_{14} SYSTEM

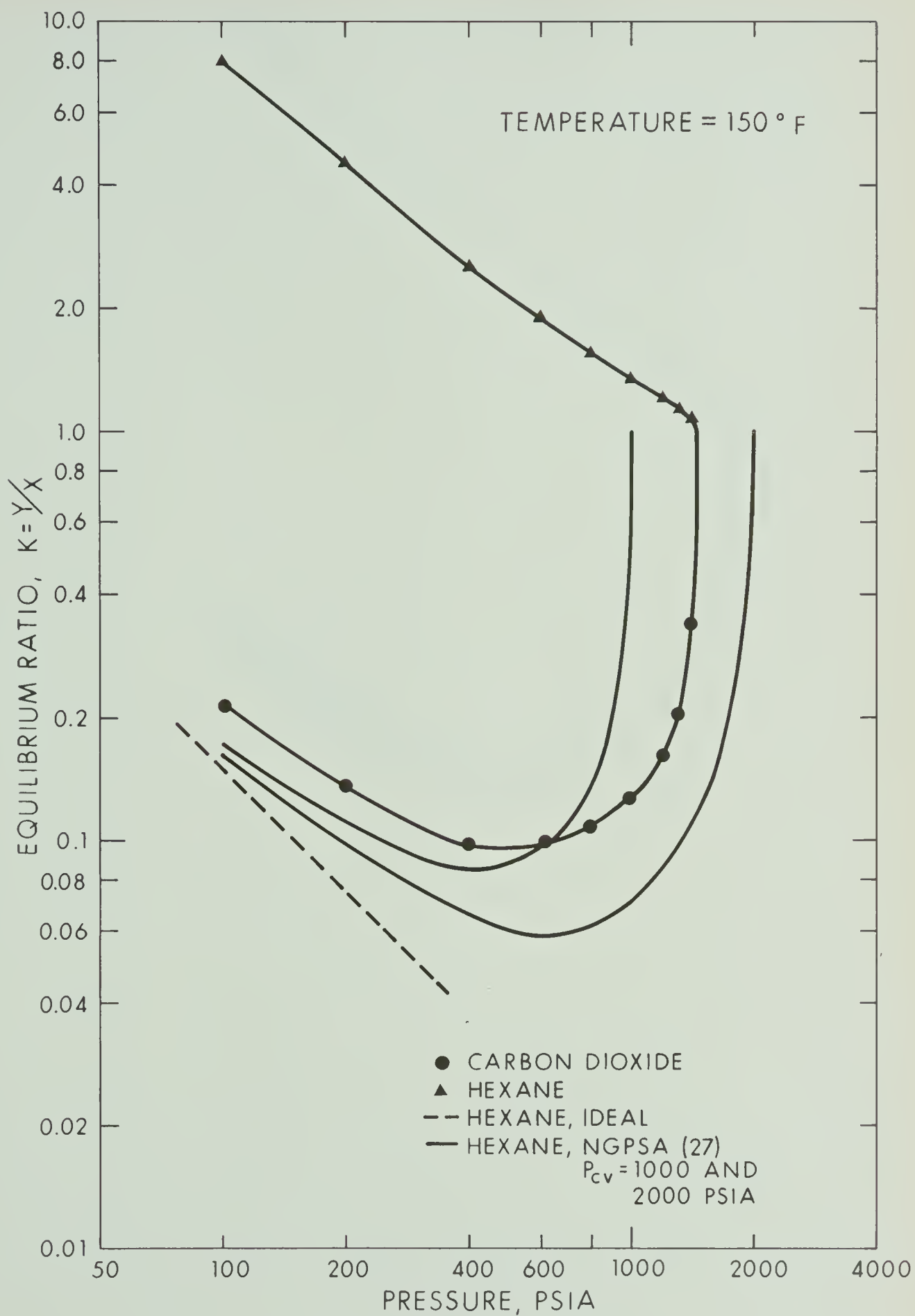


FIG.12 EQUILIBRIUM RATIOS FOR CO_2 - n - C_6H_{14} SYSTEMS

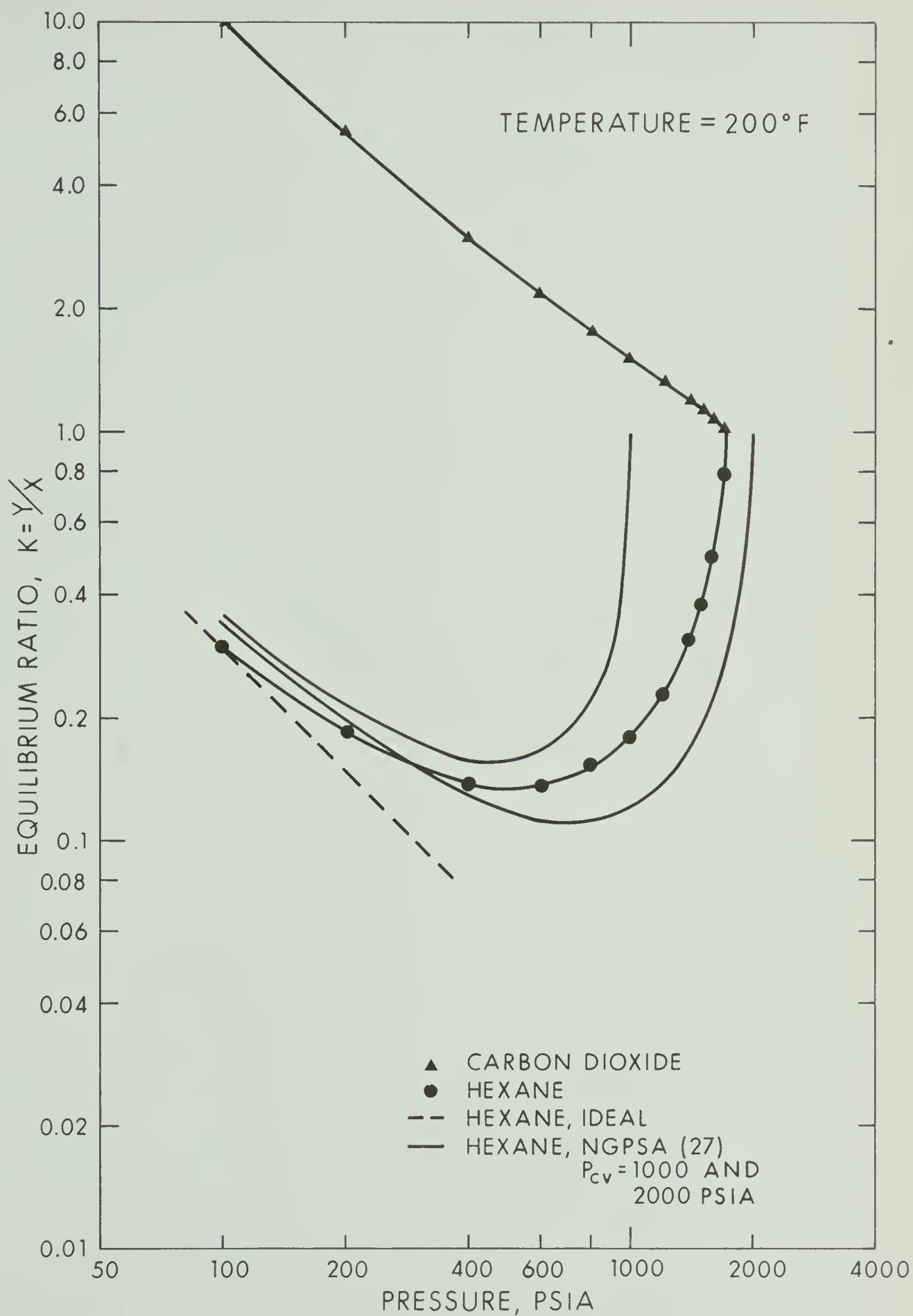


FIG.13 EQUILIBRIUM RATIOS FOR CO_2 - n - C_6H_{14} SYSTEM

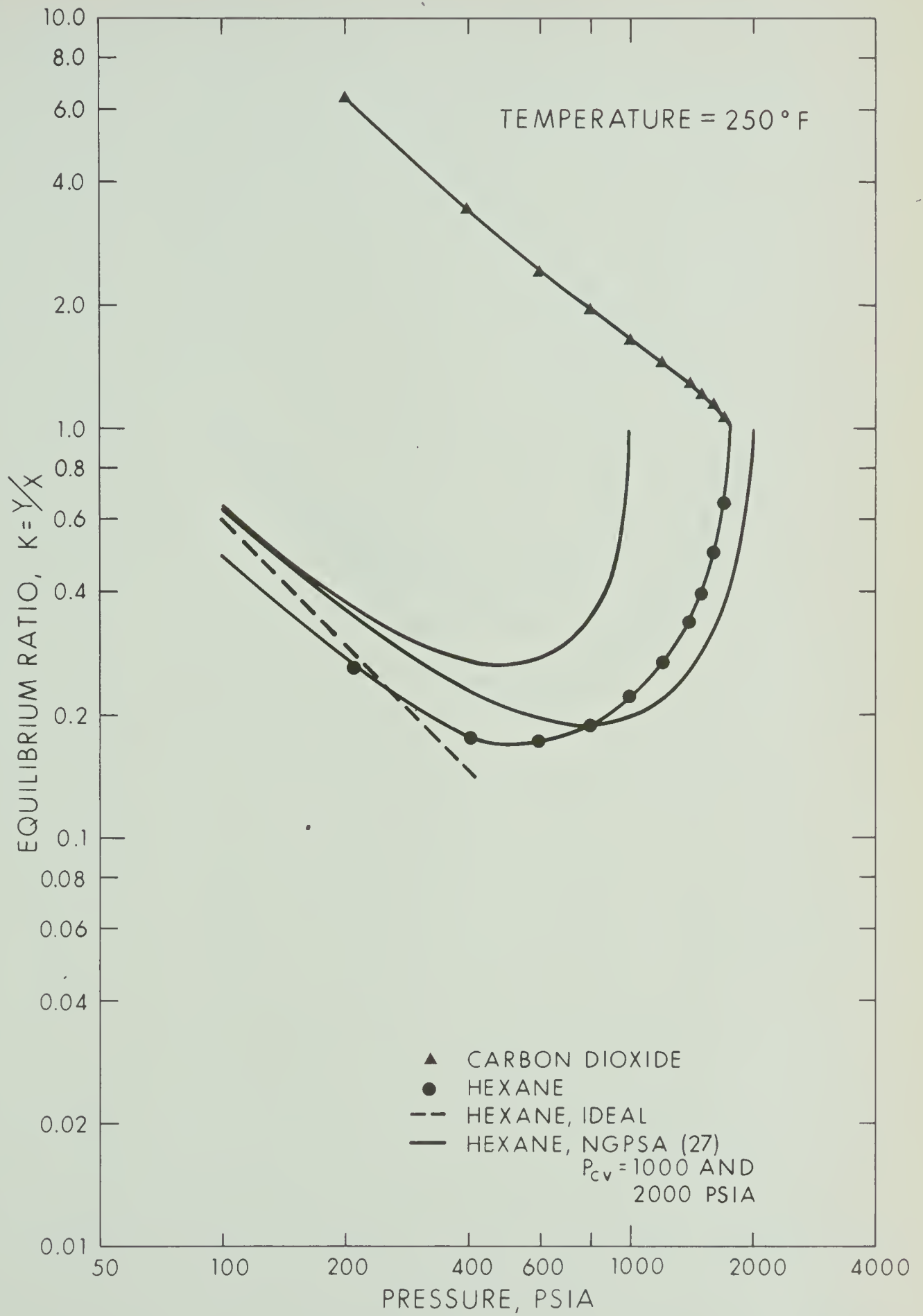


FIG.14 EQUILIBRIUM RATIOS FOR CO_2 - n - C_6H_{14} SYSTEM

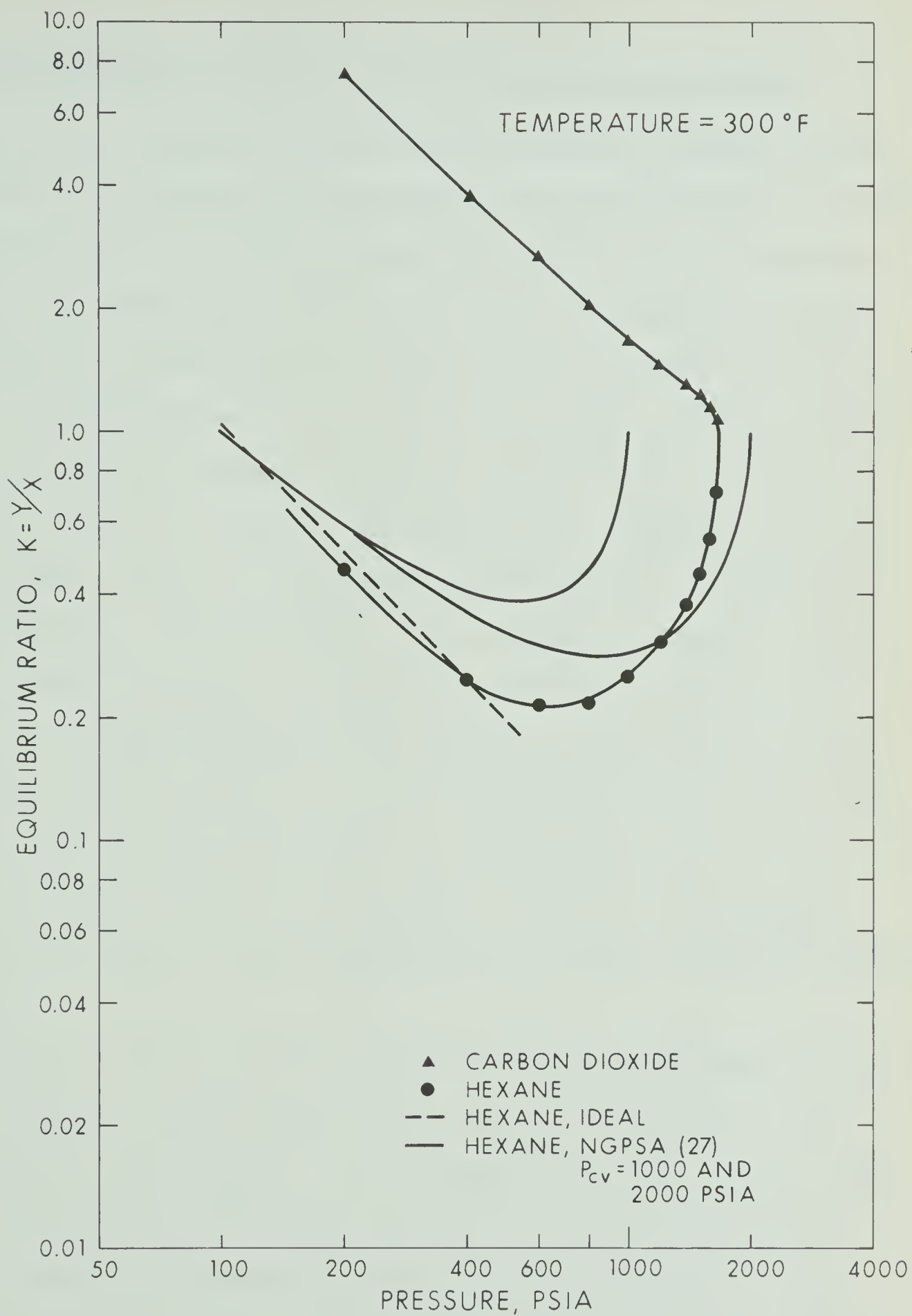


FIG.15 EQUILIBRIUM RATIOS FOR CO₂-n-C₆H₁₄ SYSTEM

VI. DISCUSSION OF RESULTS

A. Phase Behavior of the Carbon Dioxide-n-Hexane System

The phase behavior of the carbon dioxide-n-hexane system observed in this study is consistent with the behavior of other n-paraffin-carbon dioxide systems reported in the literature. Due to the temperature limitation of the experimental apparatus, complete phase envelopes could not be obtained for mixtures containing more than 15 percent n-hexane. These mixtures, at low pressures, exhibit dew point curves which, as shown in Figure 4, are very slightly inclined to the temperature axis. Thus a large change in the system temperature is accompanied by a relatively small change in the dew point pressure. As the mixtures get richer in carbon dioxide, the slope of the dew point curve progressively increases to the extent that at very high concentrations of carbon dioxide the dew point line becomes very slightly inclined to the pressure axis. For these mixtures, therefore, a slight increase in the system temperature causes a very significant increase in the dew point pressure.

Figure 3 shows that for mixtures richer in carbon dioxide the constant percent liquid lines are well separated in the low percent liquid region. For greater than 50% liquid, they are very narrowly spaced and lie close to the bubble point curve. The data presented in Table 2 of the appendix show, on the other hand, that for mixtures containing higher amounts of n-hexane, the lines are more evenly spaced.

The critical locus has some uncertainties for temperatures above 300°F. Below this temperature, the critical locus was defined by direct observation of the critical opalescence for each mixture aided by extrapolation of the constant percent liquid lines.

B. Equilibrium Ratios

(1) N-Hexane

The K-values for n-hexane obtained in this study are compared in Figures 11 to 15 with the ideal equilibrium ratios as well as with the K-values obtained from the NGPSA Engineering Data Book⁽²⁷⁾. At temperatures of 100 and 150°F, the experimental K-values are much higher than the NGPSA and the ideal K-values. The agreement between the NGPSA and experimental K-values is good at 200°F, but for pressures higher than 100 psia, the experimental values are higher than the ideal K-values. At 250°F, the experimental K-values are lower than the ideal K-values for pressures up to 250 psia. At higher pressures, this trend is reversed. The NGPSA K-values at 250°F are always higher than the experimental K-values. The agreement between the experimental and ideal K-values at 300°F is good for pressures up to 400 psia. For pressures greater than 100 psia at this temperature the experimental values are lower than the NGPSA K-values. Thus, as the system temperature increases n-hexane K-values tend to become ideal in the low pressure region.

(2) Carbon Dioxide

A comparison between the experimental K-values and the ideal K-values for carbon dioxide was not made because this component exists in a hypothetical state at all temperatures of this investigation. The NGPSA Engineering Data Book presents the K-values for this component only at a convergence pressure of 4000 psia. The convergence pressure in all mixtures of this work was less than 1800 psia.

In view of the extensive use of the NGPSA Engineering Data Book as a source of K-values, it was considered useful to prepare K-value charts for carbon dioxide at convergence pressures in the range 1000 to 2000 psia. All the K-value data available from the literature were compiled. For the binary systems, the convergence pressure was obtained by the intersection of the critical locus by the system temperature ordinate on a pressure-temperature diagram. The method of Lenoir and White⁽²³⁾ was utilized to calculate the convergence pressure of the ternary system. All other systems with a greater number of components had convergence pressures much higher than the region of interest. The paraffin hydrocarbon-non-hydrocarbon systems included in the compilation were those in which carbon dioxide was the only non-hydrocarbon component. The sources of the data taken from the literature were the following:

System	Author	Reference
C_1-CO_2	Donnelly and Katz	9
$n-C_4-CO_2$	Poettmann and Katz	29
	Olds, Reamer, Sage and Lacey	28
$n-C_5-CO_2$	Poettmann and Katz	29
$n-C_{10}-CO_2$	Reamer and Sage	33
$C_1-CO_2-n-C_4$	Saxena and Robinson	37

The data on binary systems of carbon dioxide with ethane and propane were not used because the convergence pressures in these systems were lower than the region of interest.

Charts were prepared at convergence pressures of 1200, 1450, and 1700 psia and the results are presented in Figures 16 to 18 respectively. At convergence pressures of 1450 and 1700 psia, the K-value isotherms are similar in shape to those presented by the NGPSA⁽²⁷⁾ for a convergence pressure of 4000 psia. The K-values increase, as can be expected, with increasing temperatures and with increasing convergence pressures.

At the convergence pressure of 1200 psia, the K-values for a temperature of 100°F and above are not consistent with their behavior at the higher convergence pressures. At 200°F and 900 psia for example, contrary to expected behavior, the carbon dioxide K-values are the same at convergence pressures of 1200 and 1450 psia. For pressures lower than 900 psia then K-values corresponding to 1200 psia convergence pressure are, in fact, higher than those for 1450 psia. As another example, the

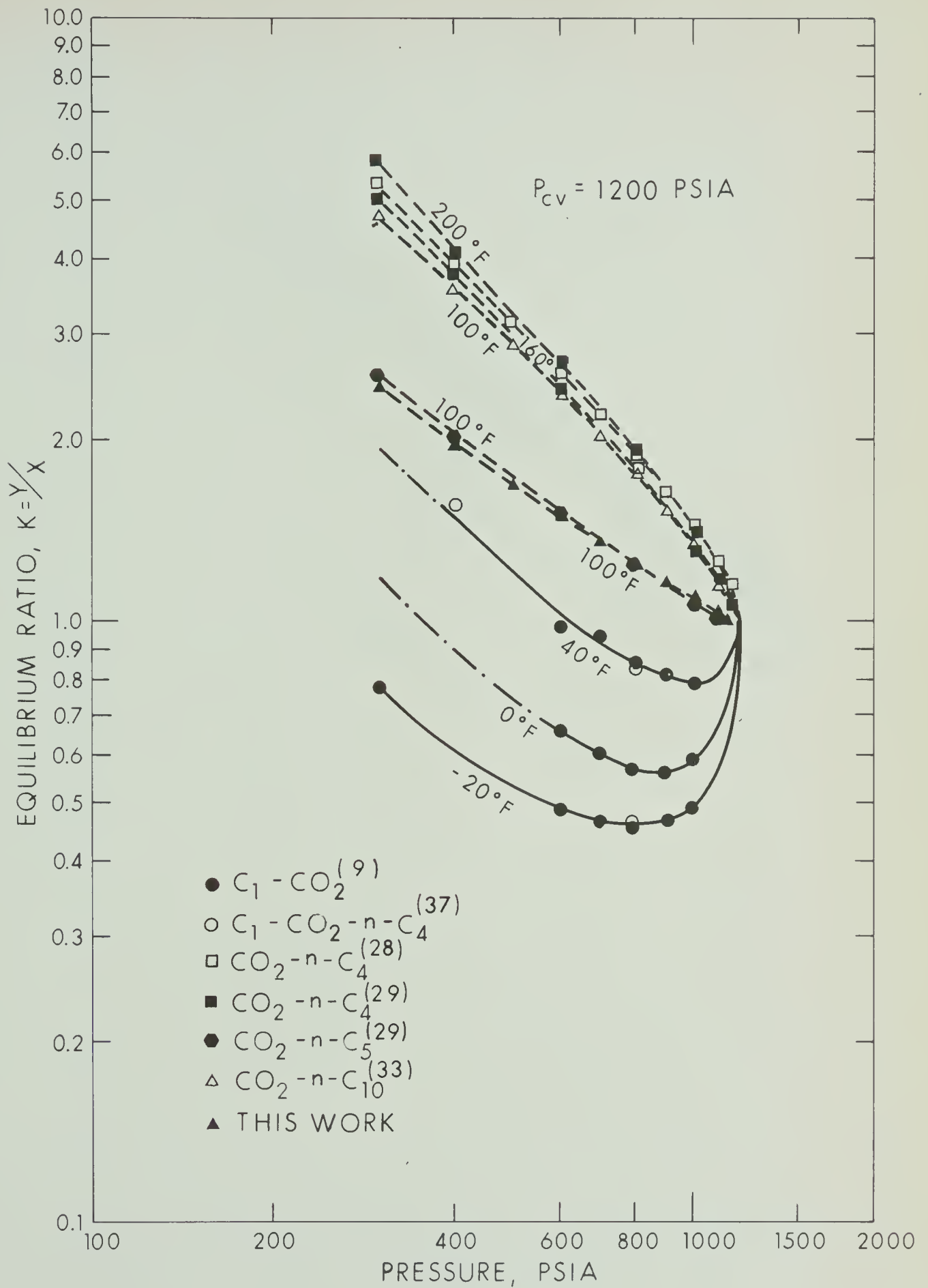


FIG.16 EQUILIBRIUM RATIOS FOR CO_2 IN
n-PARAFFIN HYDROCARBON SYSTEMS

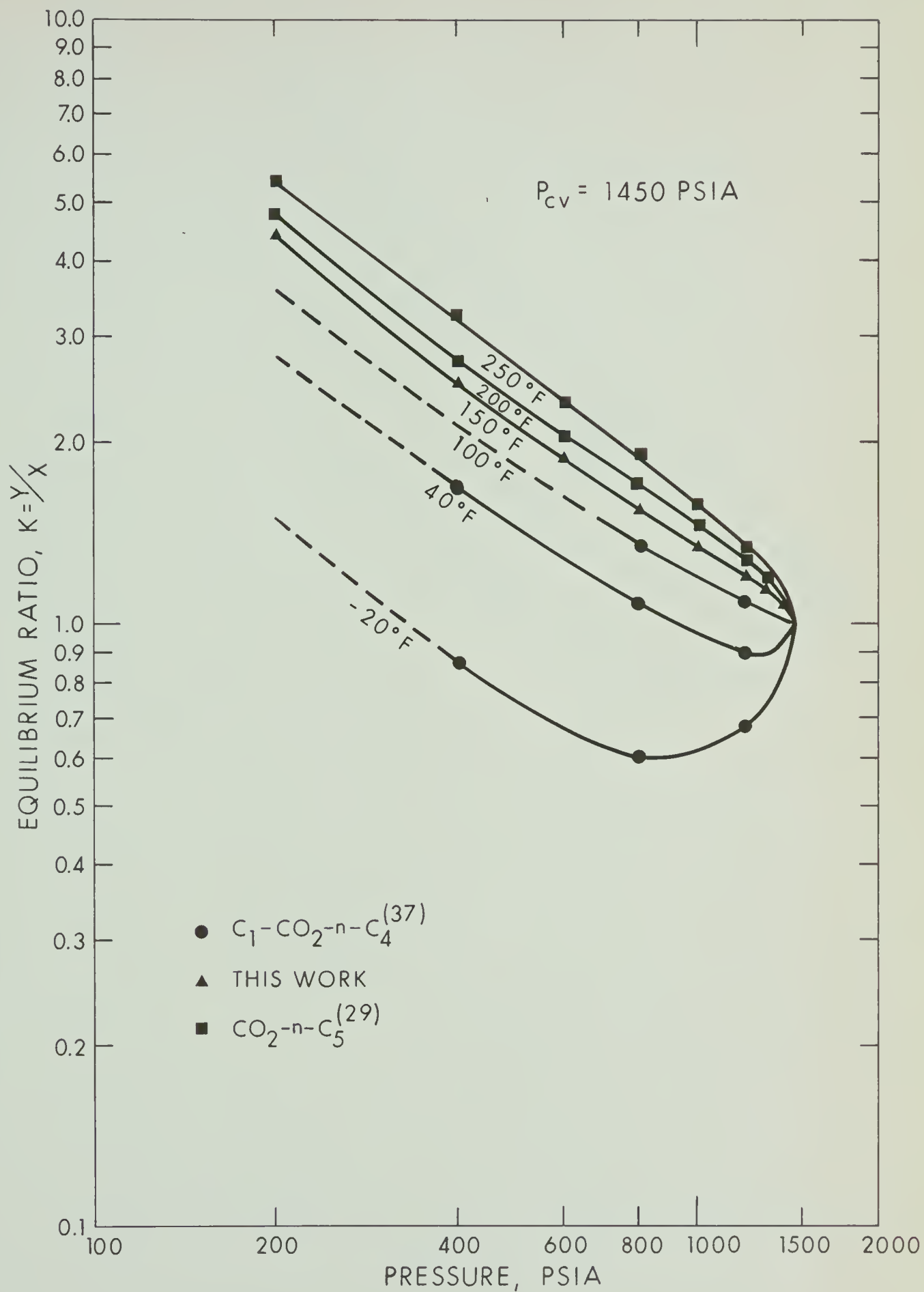


FIG.17 EQUILIBRIUM RATIOS FOR CO_2 IN n -PARAFFIN HYDROCARBON SYSTEMS

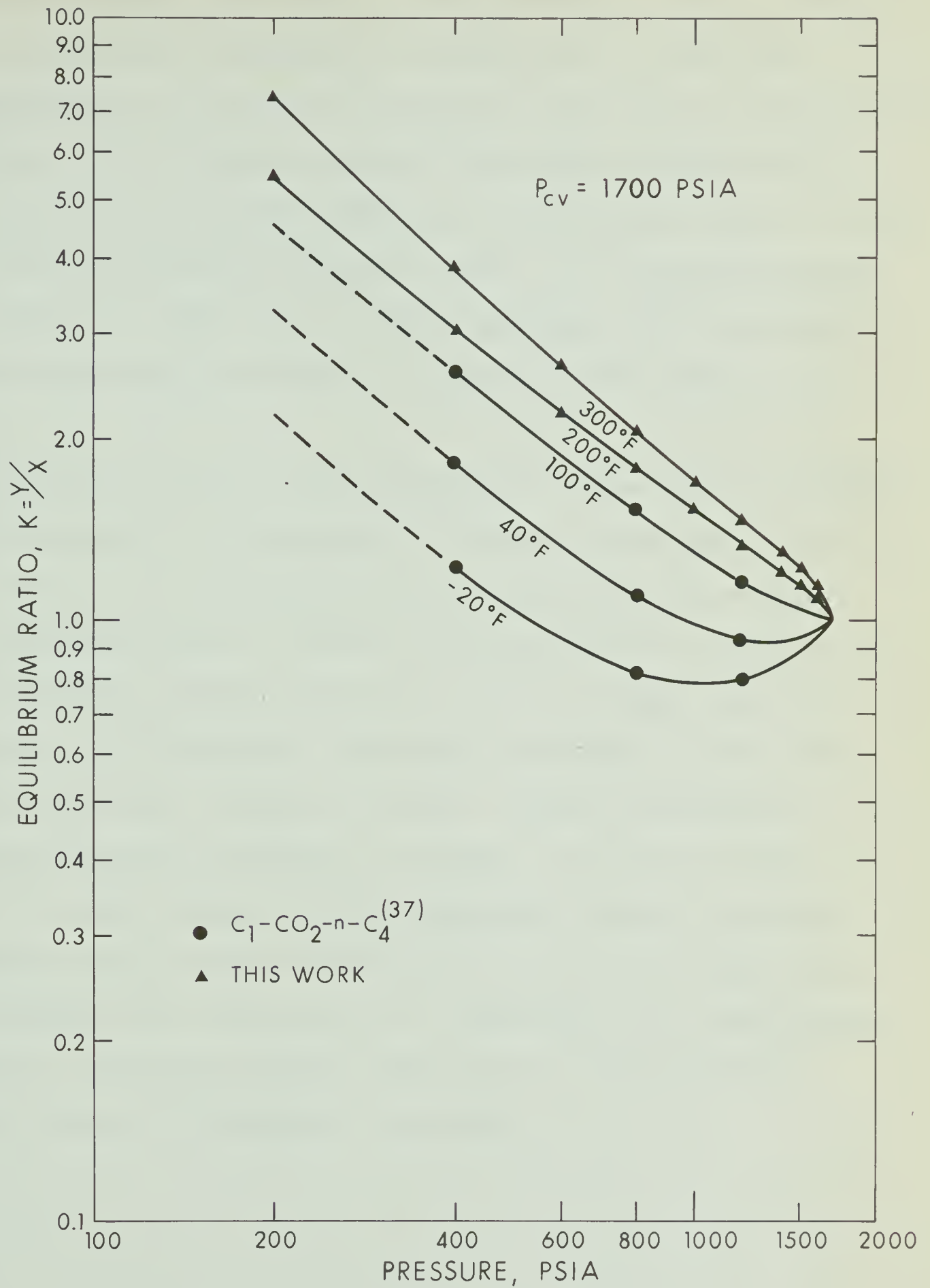


FIG.18 EQUILIBRIUM RATIOS FOR CO_2 IN
n-PARAFFIN HYDROCARBON SYSTEMS

K-values obtained from data on carbon dioxide binary systems with n-hexane and n-decane at a temperature of 100°F and corresponding to 1200 psia convergence pressure are significantly different. The K-values obtained from the n-decane binary system are so much higher that they lie close to those at 160°F taken from the data on n-butane binary. At low temperatures, for example at -20°F , the K-values increase with increasing convergence pressures which is contrary to the expected behavior.

This may be due to inconsistencies in the data of various authors utilized in preparation of these charts, but on the other hand it is also possible that the concept of convergence pressure fails to account for the effect of composition adequately in the region enclosed by dotted lines in Figure 16. To completely understand the cause of this odd behavior of carbon dioxide K-values, further information at low convergence pressures is needed. It would be necessary to study ternary or multicomponent systems in order to provide the necessary K-value data which would simultaneously satisfy the requirements of temperature and convergence pressure. In binary systems, temperature and convergence pressure are not independent variables.

VII. CONCLUSIONS

1. Modifications in the heating system for the equipment and in the material of construction for the heating jacket made it suitable for use up to temperatures 300°F . The modified equipment was used to study vapor-liquid equilibria in the carbon dioxide-n-hexane system at temperatures of 100, 150, 200, 250, and 300°F . The five mixtures studied contained 94.9, 90.7, 84.6, 75.7 and 52.5 mole percent carbon dioxide.
2. The experimental data thus obtained made it possible to define the phase diagram for this system in the experiment range 100 to 300°F . The phenomena of critical opalescence observed for some mixtures of this study proved to be a useful aid in the definition of the binary critical locus.
3. It was possible to calculate the K-ratios for carbon dioxide and n-hexane from the experimental data. The comparison of experimental K-values for n-hexane with the ideal K-values and with those obtained from the NGPSA Engineering Data Book showed that the n-hexane K-values get closer to ideal K-values as the system temperature increases. The agreement with the NGPSA K-values was good at 200°F . At temperatures of 100 and 150°F the experimental K-values were higher than NGPSA K-values but at 250 and 300°F this trend was reversed.
4. The K-values for carbon dioxide obtainable from the literature were utilized in preparing charts for this component similar to those presented in the NGPSA Engineering Data Book. These charts indicate that additional information is necessary on K-values of carbon dioxide in multicomponent paraffin hydrocarbon mixtures before any useful generalization on K-values of carbon dioxide can be made.

NOMENCLATURE

C	composition parameters based on mole fractions
G	molar free energy
K	equilibrium ratio
M	composition parameter based on mass fractions
N	total number of moles of a component
P	total pressure of system
R	gas constant
T	temperature of system
V	molal volume
f	fugacity of a component
m	weight fractions
n	number of components in the system
p	partial pressure of a component
p^V	vapor pressure of a component
x	mole fraction in liquid phase
y	mole fraction in vapor phase

Greek Letters

μ	chemical potential
$\phi \phi' \phi'' \phi'''$	denotes a function of variables
γ	activity coefficient

Subscripts

i	i^{th} component
CV	convergence
is	ideal solution property

Superscripts

V vapor phase

L liquid phase

- a bar at the top denotes the value of a
property in a mixture

REFERENCES CITED

1. Akers, W.W., Kelley, R.E., and Lipscomb, T.G., Ind. Eng. Chem., 46, 2535 (1954).
2. Allen, C., Ind, Eng. Chem., 22, 608 (1930).
3. Benedict, M., Johnson, C.A., Solomon, E., and Rubin, L.C., Trans. A.I. Ch.E., 41, 371 (1945).
4. Cajander, B.C., Hipkin, H.G., and Lenoir, J.M., Chem. Eng. Data, 5, 251 (1960).
5. Carlson, H.C., and Colburn, A.P., Ind. Eng. Chem., 34, 581 (1942).
6. Carter, R.T., Sage, B.H., Lacey, W.N., Am. Inst. Mining Met. Engrs. Tech. Pub., 1250 (Oct., 1940)
7. Colburn, A.P., and Schoenborn, E.M., Trans. A.I.Ch.E., 41, 421 (1945).
8. Cramer, F., Chem. Ing. Tech., 27, 484 (1955).
9. Donnelly, H.G., and Katz, D.L., Ind Eng. Chem., 46, 511 (1954).
10. Ewanchyna, J.E., and Ambridge, C., Can. J. Chem. Eng., 36, 19 (1958).
11. Gerster, J.A., Mertes, T.S., and Colburn, A.P., Ind. Eng. Chem., 39, 797 (1947).
12. Gibbs, J.W., "Collected Works", Vol. I, 55-345, Longmans, Green and Co. Inc., New York (1931).
13. Hadden, S.T., Chem. Eng. Prog., 44, 37, 135 (1948).
14. Hadden, S.T., Chem Eng Prog Symp. Ser., 49, (7), 53 (1953).
15. Hadden, S.T., and Grayson, H.C., Pet. Ref., 40, (9), 207 (1961).
16. Hutton, J.M., "Hydrates of the Methane-Carbon Dioxide-Hydrogen Sulphide System", M.Sc. Thesis, Library, University of Alberta, Edmonton, Canada. (1965).
17. Jacoby, R.H., and Rzasa, M.J., Pet. Trans. A.I.M.E., 198, 225 (1953).

18. Kelso, E.A., and Felsing, W.A., J. Am. Chem. Soc., 62, 3132 (1940).
19. Kelso, E.A., and Felsing, W.A., Ind. Eng. Chem., 34, 161 (1942).
20. Kuenen, J.P., Phil. Mag., 44, 174 (1897).
21. Kuenen, J.P., Z. Physik, Chem., 24, 667 (1897).
22. Kuenen, J.P., and Robson, W.G., Phil. Mag., 4, 116 (1902).
23. Lenoir, J.M., and White, G.A., Pet. Ref., 37, (3), 173 (1958).
24. Lewis, G.N., and Randall, M., "Thermodynamics", McGraw Hill Book Co. New York (1923).
25. Margules, M., Sitzber. Akad, Wiss. Wien, Math.-naturw. Kl., 104, 1243 (1895).
26. Muskat, M., "Physical Principles of Oil Production", McGraw Hill Book Co., New York (1949).
27. NGPSA Engineering Data Book, Tulsa, Okla. (1967).
28. Olds, R.H., Reamer H.H., Sage, B.H., and Lacey, W.N., Ind. Eng. Chem., 41, 475 (1949).
29. Poettmann, F.H., and Katz, D.L., *ibid*, 37, 847 (1945).
30. Poettmann, F.H., and Katz, D.L., *ibid*, 38, 530 (1946).
31. Poettmann, F.H., and Katz, D.L., Trans. A.I.M.E., 192, 141 (1951).
32. Reamer, H.H. Sage, B.H., and Lacey, W.N., Ind. Eng. Chem., 43, 2515 (1951).
33. Reamer, H.H., and Sage, B.H., J. Chem. Eng. Data, 8, (4), 508 (1963).
34. Redlich, O., and Kister, A.T., Ind. Eng. Chem., 40, 345 (1948).
35. Roof, J.G., and Baron, J.D., J. Chem. Eng. Data, 12, 292 (1967).
36. Rossini, F.D., and Pitzer, K.S., "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds", Carnegie Press, Pittsburgh (1953).

37. Saxena, A.C., and Robinson, D.B., in press.
38. Scatchard, G., Chem. Rev., 44, 7 (1949).
39. Scatchard, G., and Hamer, N.J., J. Am. Chem. Soc., 57,
1805 (1935).
40. Scatchard, G., and Raymond, C.L., *ibid*, 60, 1278 (1938).
41. Smith, K.A., and Watson, K.M., Chem. Eng. Progr., 45,
494 (1949).
42. Souders, M., Selheimer, C.W., and Brown, G.G., Ind. Eng.
Chem., 24, 517 (1932).
43. Sweigert, R.L., Weber, P., and Allen, R.L., *ibid*, 38,
185 (1946).
44. Van Laar, J.J., Z. Physik. Chem., 72, 723 (1910).
45. Van Laar, J.J., *ibid*, 83, 599 (1913).
46. Wang, R.H., and McKetta, J.J., J. Chem. and Eng. Data,
9, 30 (1964).
47. Winn, F.W., Chem. Eng. Progr. Symp. Ser., 48, (2), 121
(1952).
48. Wohl, K., Trans. A.I.Ch.E., 42, 215 (1946).

A P P E N D I X

Table 1

Experimental Dew Point and Bubble Point Data
for Carbon Dioxide-n-Hexane System

Mixture Composition = 94.9 mole percent CO₂

<u>Temperature °F</u>	<u>Dew Point Pressure, Psia.</u>	<u>Bubble Point Pressure, Psia.</u>
100.0	305	1067
121.0	385	1256
129.3	425,1320	-
150.0	532,1432	-
180.0	865,1365	-

Mixture Composition = 90.7 mole percent CO₂

100.3	152	985
139.6	205	1355
161.2	245,1513	-
180.0	325,1615	-
200.3	450,1700	-
220.0	675,1665	-

Mixture Composition = 84.6 mole percent CO₂

100.0	90	904
148.6	135	1285
199.0	210	1590
252.0	315	1720
298.6	480,1672	-

Table 1 (continued)

Mixture Composition = 75.7 mole percent CO₂

<u>Temperature</u> <u>°F</u>	<u>Dew Point</u> <u>Pressure, Psia.</u>	<u>Bubble Point</u> <u>Pressure, Psia.</u>
100.3	45	740
151.3	80	1072
201.0	115	1345
250.3	205	1535
301.3	330	1585

Mixture Composition = 52.5 mole percent CO₂

100.0	15	440
149.0	25	630
200.6	47	815
250.0	95	925
299.0	180	1000

Table 2

Experimental Percent Liquid Data for Carbon Dioxide-

n-Hexane System

Mixture Composition = 94.9 mole percent CO₂

Temperature = 100°F

Pressure, Psia.	Liquid Volume, ml.	System Volume, ml.	Percent Liquid
1060	8.83	11.32	78.00
1052	7.74	12.56	61.62
1040	6.93	13.63	50.84
1027	5.89	15.17	38.83
1009	4.86	16.89	28.77
985	3.85	19.35	19.90
957	3.09	22.18	13.93
918	2.41	25.60	9.41
871	2.00	29.60	6.76
819	1.64	33.75	4.86
734	1.37	41.53	3.30
663	1.23	48.98	2.51
600	1.15	56.85	2.02
547	1.1	65.0	1.69
495	1.0	74.42	1.34

Temperature = 121°F

1247	4.24	7.41	57.22
1237	3.33	7.63	43.64
1219	2.68	8.31	32.25
1190	2.02	9.08	22.25
1154	1.62	9.93	16.31
1112	1.25	11.12	11.24
1052	1.02	12.72	8.02
973	0.90	14.90	6.04
904	0.74	17.30	4.28
815	0.72	20.4	3.53
723	0.70	24.52	2.85
617	0.59	30.65	1.92
541	0.50	36.52	1.37

Table 2 (continued)

Pressure, Psia.	Liquid Volume, ml.	System Volume, ml.	Percent Liquid
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Temperature = 129.3°F

1319	0.63	12.22	5.15
1319	1.67	12.22	13.67
1315	2.29	12.25	18.69
1310	2.49	12.30	20.24
1305	2.46	12.35	19.92
1298	2.45	12.66	19.35
1275	2.28	13.46	16.94
1255	2.00	14.10	14.18
1220	1.72	15.42	11.15
1172	1.44	17.23	8.36
1110	1.26	19.61	6.42
1027	1.18	23.18	5.09
932	1.02	27.38	3.72
812	0.89	33.43	2.66
728	0.86	40.15	2.14
623	0.73	49.94	1.46

Temperature = 150°F

1413	0.27	12.86	2.10
1375	0.43	13.50	3.18
1317	0.60	14.78	4.05
1273	0.62	15.85	3.91
1173	0.65	18.70	3.47
1069	0.62	21.84	2.84
970	0.63	25.41	2.48
872	0.61	29.61	2.06
773	0.61	35.21	1.73

Mixture Composition = 90.7 mole percent CO₂

Temperature = 100.3°F

971	5.52	8.74	63.16
957	4.90	9.80	50.00
938	4.25	10.93	38.88
901	3.47	13.60	25.51
842	2.66	17.48	15.22

Table 2 (continued)

Pressure, Psia.	Liquid Volume, ml.	System Volume, ml.	Percent Liquid
783	2.15	21.55	9.98
684	1.73	28.03	6.17
581	1.54	36.11	4.26
483	1.42	46.71	3.04
394	1.36	60.76	2.24
327	1.18	76.50	1.54

Temperature = 139.6°F

1325	4.35	7.70	56.49
1290	4.01	9.76	41.09
1245	3.40	11.50	29.56
1205	3.00	12.80	23.44
1140	2.64	16.49	16.01
1015	2.15	21.55	9.98
880	1.79	28.50	6.28
747	1.60	35.50	4.51
580	1.33	45.38	2.93
440	1.17	58.27	2.01
322	0.90	76.6	1.17

Temperature = 161.2°F

1510	0.81	8.61	9.41
1505	1.45	8.70	16.67
1500	1.99	8.66	22.98
1495	2.25	8.66	25.98
1487	2.45	8.66	28.29
1480	2.45	8.66	28.29
1467	2.41	8.72	27.64
1452	2.40	8.89	27.00
1423	2.17	9.29	23.36
1367	1.88	10.07	18.67
1315	1.69	10.79	15.66
1245	1.55	12.10	12.81
1150	1.38	14.13	9.77
1020	1.10	17.02	6.46
896	1.03	20.71	4.97
769	1.03	25.43	4.05
622	0.96	34.16	2.81
469	0.91	49.16	1.85
330	0.67	77.18	0.87

Table 2 (continued)

Pressure, Psia.	Liquid Volume, ml.	System Volume, ml.	Percent Liquid
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Temperature = 180°F

1590	0.20	8.70	2.30
1550	0.54	8.74	6.18
1535	0.76	8.76	8.67
1510	0.96	8.76	10.96
1490	1.07	8.76	12.21
1465	1.03	8.80	11.70
1405	0.94	8.85	10.62
1345	0.89	8.99	9.90
1265	0.77	9.59	8.03
1160	0.62	10.22	6.07
1075	0.66	12.76	5.17
935	0.59	15.61	3.78
815	0.57	19.39	2.94
665	0.53	23.23	2.28
545	0.50	29.32	1.70

Temperature = 200.3°F

1667	0.18	9.36	1.92
1615	0.18	9.50	1.89
1570	0.32	9.79	3.27
1516	0.43	10.22	4.21
1460	0.48	10.76	4.46
1415	0.52	11.24	4.63
1315	0.56	12.36	4.53
1220	0.57	13.70	4.16
1070	0.56	16.42	3.41
919	0.54	20.09	2.69
771	0.54	25.52	2.11
621	0.42	33.57	1.25

Mixture Composition = 84.6 mole percent CO₂

Temperature = 100°F

884	7.28	10.68	68.16
868	6.88	11.83	58.15
841	6.07	13.79	44.01
810	6.10	16.10	37.88
784	5.88	18.10	32.48
729	5.31	22.25	23.86
647	4.81	28.50	16.87

Table 2 (continued)

Pressure, Psia.	Liquid Volume, ml.	System Volume, ml.	Percent Liquid
570	4.53	35.08	12.91
489	4.30	43.98	9.77
416	4.07	54.32	7.49
343	3.93	68.59	5.72
310	3.65	76.83	4.75

Temperature = 148.6°F

1240	7.65	10.70	71.49
1193	6.97	12.05	57.84
1133	6.30	13.92	45.25
1073	5.90	15.83	37.27
1010	5.55	18.05	30.74
911	4.98	21.80	22.84
817	4.67	26.29	17.76
713	4.33	31.93	13.56
567	3.99	43.09	9.25
483	3.80	53.05	7.16
415	3.84	63.80	6.01
350	3.40	77.20	4.40

Temperature = 199°F

1533	7.79	11.86	65.68
1470	6.93	12.68	54.65
1390	6.16	13.78	44.70
1307	5.595	15.225	36.74
1203	5.10	17.425	29.27
1087	4.725	20.45	23.10
963	4.37	24.17	18.08
803	3.95	30.98	12.75
695	3.70	37.40	9.89
592	3.52	45.70	7.70
501	3.27	55.85	5.85
442	3.18	65.08	4.89
384	2.69	76.49	3.51

Table 2 (continued)

Pressure, Psia.	Liquid Volume, ml.	System Volume, ml.	Percent Liquid
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Temperature = 252°F

1690	7.47	12.19	61.28
1667	6.74	12.44	54.18
1623	6.02	12.90	46.67
1535	5.19	14.02	37.02
1425	4.65	15.55	29.90
1330	4.29	17.05	25.20
1175	3.80	20.23	18.78
1015	3.54	24.50	14.45
853	3.19	30.60	10.42
717	2.83	37.84	7.48
623	2.60	45.09	5.77
569	2.33	50.49	4.61
513	2.18	57.32	3.80
457	1.89	66.52	2.84
405	1.59	77.20	2.06

Temperature = 298.6°F

1667	3.60	12.91	27.88
1660	3.75	12.96	28.93
1650	3.91	13.09	29.87
1640	3.99	13.20	30.23
1620	4.00	13.38	29.90
1597	3.97	13.58	29.23
1547	3.83	14.23	26.91
1465	3.66	15.22	24.05
1380	3.46	16.36	21.15
1273	3.21	18.12	17.71
1115	2.84	21.32	13.32
965	2.55	25.59	9.96
831	2.24	30.96	7.23
727	1.93	36.85	5.24
640	1.66	44.11	3.76
588	1.37	49.99	2.74
537	0.89	56.70	1.57

Table 2 (continued)

Pressure, Psia.	Liquid Volume, ml.	System Volume, ml.	Percent Liquid
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Mixture Composition = 75.7 mole percent CO₂

Temperature = 100.3°F

709	6.73	10.05	66.97
691	6.55	11.05	59.28
672	6.24	11.86	52.61
621	5.78	14.90	38.79
573	5.39	18.05	29.86
501	5.07	21.80	23.26
418	4.61	31.95	14.43
211	3.87	77.03	5.02

Temperature = 151.3°F

1021	6.45	9.24	69.80
962	5.96	10.50	56.76
921	5.63	11.38	49.47
844	5.24	13.33	39.31
771	4.87	15.46	31.50
670	4.64	19.42	23.89
568	4.36	24.60	17.72
454	4.04	33.71	11.98
320	3.73	52.14	7.15
230	3.28	76.83	4.27

Temperature = 201°F

1235	5.91	9.36	63.14
1147	5.29	10.23	51.71
1070	4.90	11.18	43.83
965	4.60	12.88	35.71
848	4.24	15.42	27.50
724	3.87	19.42	19.93
592	3.65	25.55	14.28
468	3.48	35.00	9.94
344	2.88	51.16	5.63
242	2.50	77.40	3.23

Table 2 (continued)

Pressure, Psia.	Liquid Volume, ml.	System Volume, ml.	Percent Liquid
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Mixture Composition = 75.7 mole percent CO₂

Temperature = 250.3°F

1453	5.86	8.82	66.44
1377	5.37	9.37	57.31
1285	4.88	9.98	48.90
1215	4.49	10.69	42.00
1097	4.12	12.11	34.02
969	3.89	14.02	27.75
826	3.47	17.22	20.15
693	3.12	21.50	14.51
569	2.88	27.79	10.36
454	2.50	37.35	6.69
349	2.10	52.20	4.02
264	1.36	74.54	1.82

Temperature = 301.3°F

1507	5.38	8.80	61.14
1443	4.86	9.16	53.06
1360	4.29	9.75	44.00
1277	3.85	10.40	37.02
1177	3.46	11.56	29.93
1043	3.22	13.28	24.25
907	2.80	15.60	17.95
775	2.49	19.00	13.10
617	2.08	25.79	8.06
476	1.47	36.96	3.98
371	0.63	52.33	1.20

Mixture Composition = 52.5 mole percent CO₂

Temperature = 100°F

370	3.50	6.80	51.47
322	3.44	8.66	39.72
266	3.15	12.53	25.14
219	3.03	15.41	19.66
175	2.94	21.16	13.89
137	2.93	28.71	10.20
100	2.74	40.92	6.69
72	2.83	56.57	5.00
55	2.54	77.10	3.29

Table 2 (continued)

Pressure, Psia.	Liquid Volume, ml.	System Volume, ml.	Percent Liquid
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Temperature = 149°F

505	2.86	5.68	50.35
455	2.76	6.49	42.53
397	2.63	7.61	34.56
329	2.55	9.90	25.76
271	2.61	13.03	20.03
221	2.39	17.28	13.83
171	2.32	23.62	9.82
130	2.28	32.62	6.99
90	2.22	48.93	4.54
59	1.94	76.65	2.53

Temperature 200.6°F

642	2.75	5.33	51.59
605	2.64	5.80	45.52
551	2.59	6.41	40.40
495	2.49	7.41	33.60
435	2.35	8.46	27.78
349	2.20	11.20	19.64
290	2.15	14.43	14.90
225	1.98	19.83	9.99
171	1.97	28.28	6.97
132	1.81	39.29	4.61
97	1.54	57.21	2.69
75	1.39	77.60	1.79

Temperature = 250°F

718	2.49	5.02	49.60
647	2.18	5.41	40.29
587	2.07	6.07	34.10
521	2.00	6.70	29.85
452	1.88	7.88	23.85
395	1.88	9.41	19.98
333	1.75	12.12	14.44
274	1.68	15.78	10.65
217	1.47	21.76	6.75
168	1.32	32.85	4.02
127	0.76	50.68	1.50

Table 2 (continued)

Pressure, Psia.	Liquid Volume, ml.	System Volume, ml.	Percent Liquid
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Temperature = 299°F

753	1.94	4.56	42.54
676	1.80	4.86	37.04
611	1.70	5.40	31.48
542	1.51	6.17	24.47
475	1.45	7.25	20.00
411	1.35	8.88	15.20
361	1.16	10.76	10.78
314	1.05	13.63	7.70
265	0.83	17.68	4.69
226	0.57	23.00	2.48

Table 3

Data on Critical Locus for Carbon Dioxide-

n-Hexane System

Composition mole percent CO ₂	Temperature, °F	Pressure, Psia.
94.9	124.5	1287
90.7	150.6	1448
84.6	291.6	1690
-	184.0	1678
-	235.6	1780

Table 4

Equilibrium Ratios for Carbon Dioxide-n-Hexane System

Temperature = 100°F

Pressure, Psia.	Equilibrium Ratios	
	Carbon Dioxide	n-hexane
100	5.810	0.1643
200	3.375	0.1033
300	2.448	0.0816
400	1.971	0.0742
500	1.681	0.0709
600	1.492	0.0693
700	1.346	0.0735
800	1.237	0.0917
900	1.156	0.1133
1000	1.083	0.1827
1100	1.021	0.4473
1140	1.00	1.0

Temperature = 150°F

100	7.950	0.2277
200	4.460	0.1350
400	2.486	0.0964
600	1.874	0.0975
800	1.539	0.1087
1000	1.332	0.1268
1200	1.196	0.1587
1300	1.139	0.2013
1400	1.082	0.3363
1448	1.0	1.0

Table 4 (continued)

Temperature = 200°F

Pressure, Psia.	Equilibrium Ratios	
	Carbon Dioxide	n-hexane
100	10.320	0.299
200	5.440	0.187
400	2.990	0.138
600	2.190	0.137
800	1.780	0.152
1000	1.519	0.180
1200	1.338	0.229
1400	1.195	0.315
1500	1.141	0.378
1600	1.087	0.506
1700	1.029	0.782
1740	1.0	1.0

Temperature = 250°F

200	6.355	0.2830
400	3.425	0.1742
600	2.413	0.1698
800	1.914	0.1886
1000	1.630	0.2232
1200	1.433	0.2688
1400	1.282	0.3355
1500	1.210	0.3953
1600	1.137	0.5000
1700	1.068	0.6607
1770	1.0	1.0

Temperature = 300°F

200	7.400	0.458
400	3.828	0.248
600	2.645	0.2075
800	2.058	0.217
1000	1.676	0.252
1200	1.454	0.303
1400	1.290	0.377
1500	1.217	0.443
1600	1.141	0.546
1650	1.075	0.7075
1672	1.0	1.0

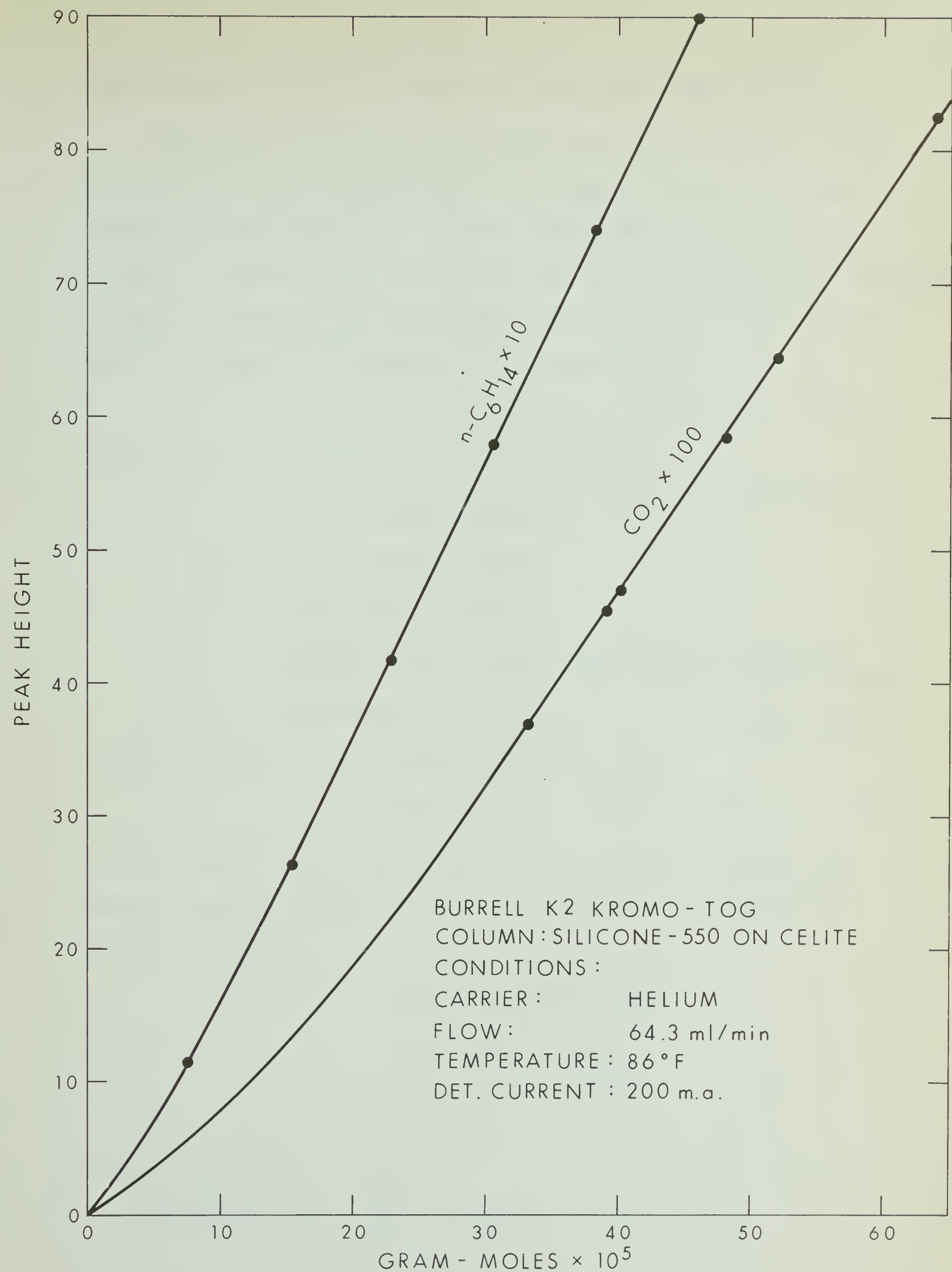


FIG. 19 CHROMATOGRAPH CALIBRATION CURVES FOR CO_2 and $n\text{-C}_6\text{H}_{14}$

Calculation of Volume Correction due to Meniscus Effects

The width of cell is 3/8" hence one can consider it as two vertical plates separated by a large distance for the purpose of calculation of volume correction due to meniscus effects. Champion and Davy have derived an equation for the curve of liquid meniscus along the side of a vertical plate in their book on Properties of Matter. The equation is

$$g\rho y^2 = 2T(1 - \sin\psi) \quad (1a)$$

Where g is acceleration due to gravity

ρ is the difference of densities of two fluids forming the meniscus

T is the surface tension

ψ is the contact angle

Y is the distance of meniscus surface from the point where liquid makes contact with the plate

If it is assumed that the liquid forms a circular arc of radius Y , then volume correction is given by

$$V_C = \frac{1}{2}(4Y^2 - \pi Y^2) \times \text{depth of cell} \quad (1b)$$

For mercury, contact angle with steel is 154° . Taking the surface tension of mercury as 460 dynes/cm, Y is given by equation (1a)

$$\begin{aligned} Y^2 &= \frac{2 \times 460(1 - \sin 154^\circ)}{980 \times (13.6 - 0.659)} \\ &= \frac{2 \times 460 \times 0.562}{980 \times (13.6 - 0.659)} \\ &= 0.0404 \text{ cm}^2 \end{aligned}$$

depth of the cell = 2.38 cms

$$\begin{aligned} \text{Therefore } V_C &= \frac{1}{2} \times 0.0404(4 - 3.14) \times 2.38 \\ &= 0.0413 \text{ c.c.} \end{aligned}$$

Similar calculations for n-hexane at 20°C gave a volume correction for hexane meniscus as 0.058 c.c. Thus, the total correction was less than 0.1 c.c. However, this correction would be even smaller at higher temperatures because the surface tension decreases with increasing temperatures. This small correction does not affect % liquid significantly even when amount of liquid present was small because in such cases, the amount of vapor phase is very large.

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